



Citation for published version:

Topolov, VY, Bowen, CR & Ermakov, IA 2016, 'Remarkable hydrostatic piezoelectric response of novel 2–0–2 composites', *Ferroelectrics, Letters Section*, vol. 43, no. 4-6, pp. 90-95.
<https://doi.org/10.1080/07315171.2016.1210978>

DOI:

[10.1080/07315171.2016.1210978](https://doi.org/10.1080/07315171.2016.1210978)

Publication date:

2016

Document Version

Early version, also known as pre-print

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REMARKABLE HYDROSTATIC PIEZOELECTRIC RESPONSE OF NOVEL 2–0–2 COMPOSITES

VITALY YU. TOPOLOV*

Department of Physics, Southern Federal University, Rostov-on-Don, 344090, Russia

CHRISTOPHER R. BOWEN

Department of Mechanical Engineering, University of Bath, Bath BA2 7AY, United Kingdom

IVAN A. ERMAKOV

Department of Physics, Southern Federal University, Rostov-on-Don, 344090, Russia

This is the first study of the significant influence of the 0–3 ceramic / polymer layer on the hydrostatic piezoelectric parameters of novel 2–0–2 relaxor-ferroelectric single crystal / ferroelectric ceramic / polymer composites. Examples of the performance of two 2–0–2 composites based on domain-engineered single crystals are analysed by taking into account the elastic anisotropy of the 0–3 ceramic/polymer layers with changes in the volume fraction of ceramic inclusions and their aspect ratio. The unique feature of the hydrostatic properties of the studied 2–0–2 composites consists in their large values of piezoelectric coefficients $d_h^* \approx 1$ nC/N and $e_h^* \approx 20$ C/m², squared figure of merit $d_h^* g_h^* \sim 10^{-10}$ Pa⁻¹, and electromechanical coupling factor $k_h^* \approx 0.7$.

Keywords: Piezo-composite based on relaxor-ferroelectric; Hydrostatic piezoelectric coefficient; Elastic properties; Aspect ratio

Domain-engineered single crystals (SCs) of relaxor-ferroelectric $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3-x}\text{PbTiO}_3$ (PMN- x PT) and $(1-y)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_{3-y}\text{PbTiO}_3$ (PZN- y PT) solid solutions are advanced materials that exhibit a range of intriguing properties such as high piezoelectric activity, large electromechanical coupling factors (ECFs) and dielectric permittivities^{1,2} near the morphotropic phase boundary. The aforementioned SCs are used as highly effective components of modern piezo-composites³⁻⁵ that are applied in piezotechnical devices for applications including hydroacoustic, transducer and energy-harvesting applications. Among the piezo-composites based on either PMN- x PT or PZN- y PT SCs, of specific interest are two-component (SC/polymer) materials^{1,3-5} 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

* Email: vutopolov@sfnedu.ru

samples of a 2–2-type PZT ceramic / heterogeneous polymer composite were prepared⁹ 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_t^* 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 $\mathbf{P}_s^{(1)}$ and main crystallographic axes $X||OX_1$, $Y||OX_2$ and $Z||\mathbf{P}_s^{(1)}||OX_3$.

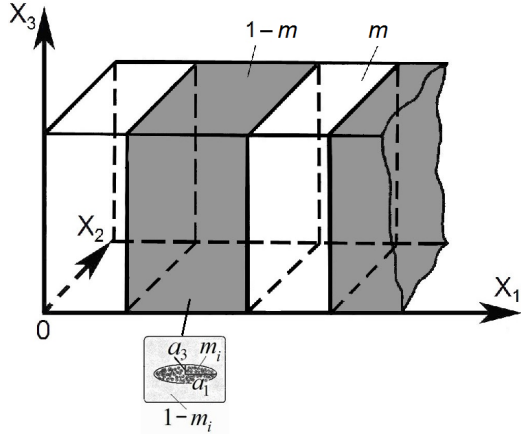


Fig. 1. Schematic of the 2–0–2 SC/ceramic/polymer composite. $(X_1X_2X_3)$ is a rectangular co-ordinate system, m and $1-m$ are volume fractions of the SC and ceramic/polymer layers, respectively, m_i is the volume fraction of isolated ceramic inclusions in the polymer medium, a_1 and a_3 are semi-axes of each inclusion. Electrodes are applied parallel to the (X_1OX_2) plane.

The second type 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 co-ordinate system $(X_1X_2X_3)$, and $\rho_i=a_1/a_3$ 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_1 . The ceramic inclusions occupy sites of a simple tetragonal lattice with unit-cell vectors parallel to the OX_k 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 method⁵ 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 method⁵ 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 ρ_i . Hereafter we analyse the following hydrostatic parameters of the composite: its piezoelectric coefficients

$$d_h^* = d_{33}^* + d_{32}^* + d_{31}^* \text{ and } e_h^* = e_{33}^* + e_{32}^* + e_{31}^*, \quad (1)$$

squared figure of merit (SFM)

$$(Q_h^*)^2 = d_h^* g_h^*, \quad (2)$$

and ECF

$$k_h^* = d_h^* / (\varepsilon_{33}^{*\sigma} s_h^{*E})^{1/2}. \quad (3)$$

In Eq.(2), $g_h^* = g_{33}^* + g_{32}^* + g_{31}^*$ is the hydrostatic piezoelectric

coefficient. In Eq.(3), $\varepsilon_{33}^{*\sigma}$ is dielectric permittivity at mechanical stress $\sigma = \text{const}$, and

$$s_h^{*E} = \sum_{a=1}^3 \sum_{b=1}^3 s_{ab}^{*E}$$

is hydrostatic elastic compliance at electric field $E = \text{const}$.

The piezoelectric coefficients d_h^* and g_h^* from Eqs. (1) and (2) describe the piezoelectric activity and sensitivity, respectively, under hydrostatic loading. The piezoelectric coefficient e_h^* from Eq.(1) is of interest to take into account sound propagation from an acoustic antenna in water. The SFM $(Q_h^*)^2$ from Eq.(2) characterises the sensor signal-to-noise ratio under hydrostatic loading. The ECF k_h^* from Eq.(3) describes the effectiveness of the energy conversion under hydrostatic loading.

Among the components of interest in terms 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 PbTiO₃ 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 (ρ_i) dependences of the effective parameters (1)–(3) of the 2–0–2 composite, we use electromechanical constants of the PMN–0.33PT¹⁰ and PZN–0.08PT¹¹ SCs, modified PbTiO₃ ceramic¹² and polyethylene^{13,14} at the Poisson's ratio 0.20. As follows from our evaluations, the 0–3 layer exhibits a low piezoelectric activity⁸ due to the isolated ceramic inclusions at $0 < m_i \leq 0.3$ and $0.01 \leq \rho_i \leq 100$. 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 $|d_{3j}^{(m)}| < 10$ 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 $\max d_h^*$ of the 2–0–2 composite (Fig. 2a, curves 1–8 and 2a) and $\max d_h^*$ of the 2–2 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 $\max d_h^*$ increases with increasing the aspect ratio ρ_i at $m_i = \text{const}$ (cf. curves 1 and 8 in Fig. 2a). In the presence of heavily oblate ceramic inclusions ($\rho_i = 100$), we obtain $\max d_h^* \approx 1000$ pC/N for both the 2–0–2 composites (Fig. 3a and 3b). As follows from experimental data,^{10,11} $d_h^{(1)} = -20$ 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

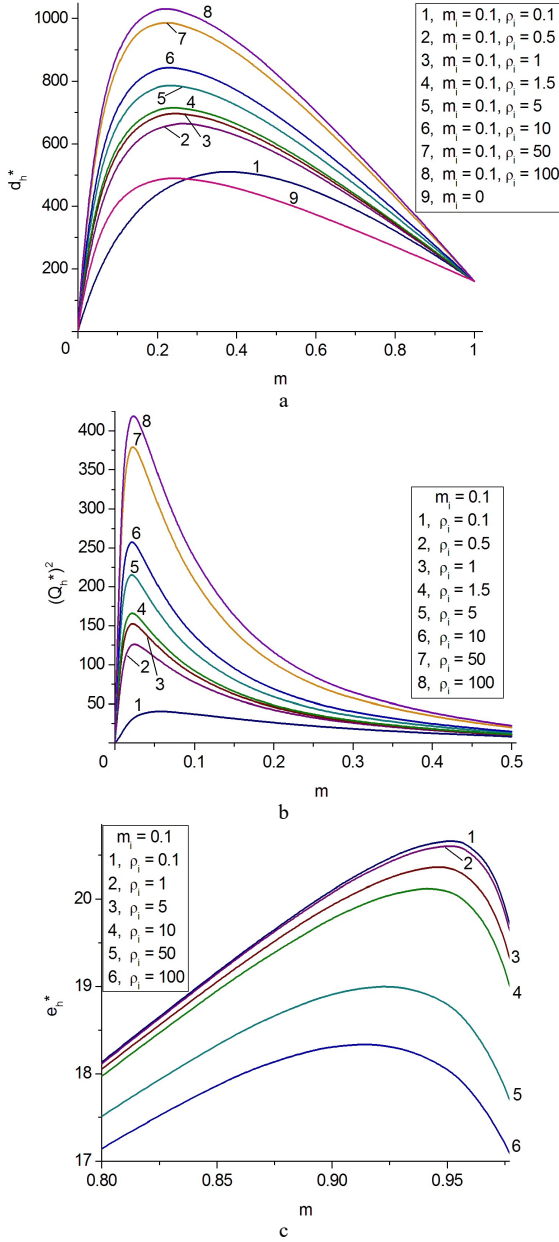


Fig. 2. Volume-fraction (m) dependence of the hydrostatic piezoelectric coefficient d_h^* (a, in pC/N), hydrostatic SFM $(Q_h^*)^2$ (b, in 10^{-12} Pa^{-1}) and hydrostatic piezoelectric coefficient e_h^* (c, in C/m^2) of the 2–0–2 PMN–0.33PT SC / modified PbTiO₃ ceramic / polyethylene composite. Curve 9 in graph (a) is related to the 2–2 PMN–0.33PT SC / polyethylene composite.

difference between $\max d_h^*$ in Fig. 3a and 3b. Moreover, these maxima at $\rho_i \gg 1$ are achieved at $m \approx 0.19$. As follows from our results on the 0–3 layer, its elastic compliances $s_{ab}^{(2)}$ at $m_i = 0.19$ and $\rho_i = 100$ exhibit a large degree of anisotropy: e.g., $s_{11}^{(2)}/s_{12}^{(2)} = -5.68$, $s_{11}^{(2)}/s_{13}^{(2)} = -4.30$ and $s_{11}^{(2)}/s_{33}^{(2)} = 0.104$. The elastic compliances $s_{ab}^{(1),E}$ of the PZN–0.08PT¹¹ and PMN–0.33PT¹⁰ SCs lead to ratios $s_{11}^{(1),E}/s_{11}^{(2)} \approx s_{12}^{(1),E}/s_{12}^{(2)} \approx 1.3–1.7$ and $s_{33}^{(1),E}/s_{33}^{(2)} \approx 0.11–0.13$, and these ratios favour large values of both d_{33}^* and d_h^* . The large piezoelectric coefficient d_h^* leads to large values of the

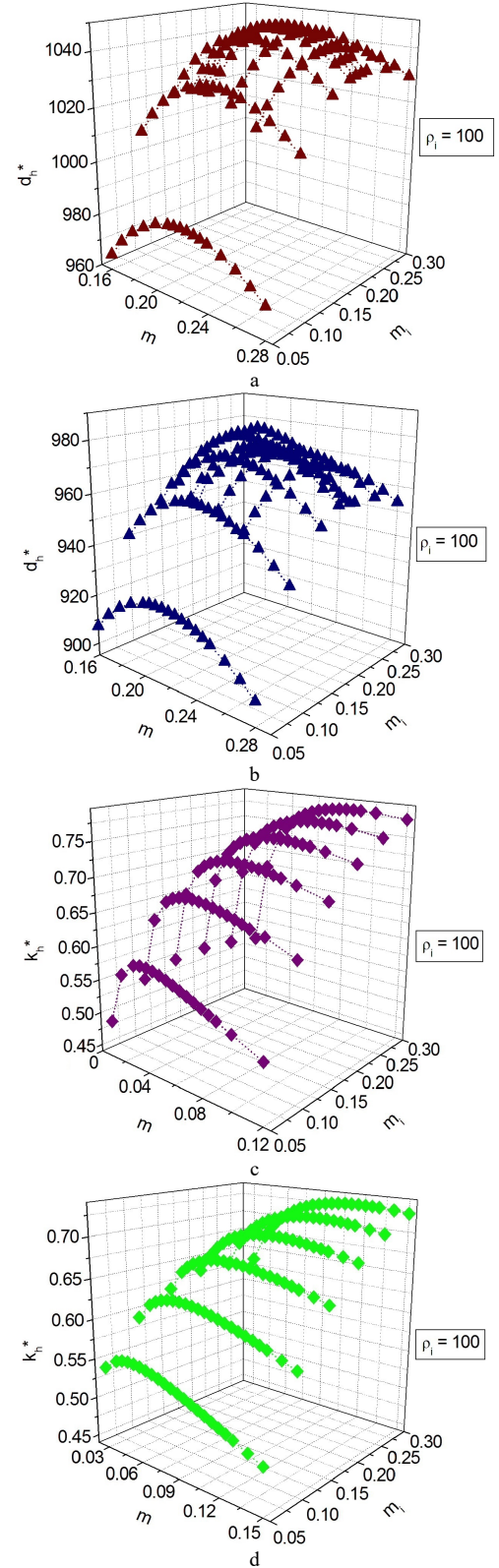


Fig. 3. Behaviour of the hydrostatic piezoelectric coefficient d_h^* (a and b, in pC/N) and hydrostatic ECF k_h^* (c and d) of the 2–0–2 PMN–0.33PT SC / modified PbTiO₃ ceramic / polyethylene composite (a and c) and 2–0–2 PZN–0.08PT SC / modified PbTiO₃ ceramic / polyethylene composite (b and d) near maxima of the parameters at $\rho_i = 100$.

SFM $(Q_h^*)^2$ (Fig. 2b) and ECF k_h^* (Fig. 3c and d), and a correlation between $\max d_h^*$, $\max[(Q_h^*)^2]$ and $\max k_h^*$ is observed. For comparison we add that the PMN–0.33PT SC¹⁰ is characterised by $(Q_h^{(1)})^2 = 3.53 \cdot 10^{-13} \text{ Pa}^{-1}$, $k_h^{(1)} = 0.167$ and $e_h^{(1)} = 15.5 \text{ C/m}^2$, and the PZN–0.08PT SC¹¹ is characterised by $(Q_h^{(1)})^2 = 5.87 \cdot 10^{-15} \text{ Pa}^{-1}$, $k_h^{(1)} = -0.0258$ and $e_h^{(1)} = 6.71 \text{ C/m}^2$. A displacement of $\max[(Q_h^*)^2]$ to smaller m values in comparison to $\max d_h^*$ (cf. Fig. 2a and 2b) is caused by a sharp $\max g_h^*$ at $m < 0.01$. Such a behaviour is a result of the strong influence⁵ of relatively small values of $\varepsilon_{33}^{*\sigma}$ on g_{3j}^* at $m \ll 1$. The sharp $\max g_h^*$ is also typical of the 2–2 SC/polymer composite.^{4,5}

In contrast to $\max d_h^*$ and $\max g_h^*$, $\max e_h^*$ is achieved at large volume fractions of SC m (Fig. 2c), and non-oblate ceramic inclusions promote larger values of e_h^* at $m = \text{const}$. The system of interfaces $x_1 = \text{const}$ (Fig. 1) and prolate ceramic inclusions in the 0–3 layers lead to decreasing $|e_{31}^*|$ and $|e_{32}^*|$ in the wide m range. As a consequence, e_{33}^* becomes the largest contribution into e_h^* , and $\max e_{33}^*$ 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_{3j}^* of the composite at $m \geq 0.9$ slowly approach $d_{3j}^{(1)}$ 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 PbTiO₃ ceramic / polyurethane composite,⁸ values of $d_h^* \sim 10^2 \text{ pC/N}$, $(Q_h^*)^2 \sim 10^{-11} \text{ Pa}^{-1}$, and $k_h^* \approx 0.5\text{--}0.6$ 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– x PT SC, values of $d_h^* = 337 \text{ pC/N}$ and $(Q_h^*)^2 = 1.6 \cdot 10^{-11} \text{ Pa}^{-1}$ 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 $e_h^* \approx 20 \text{ C/m}^2$ (Fig. 2c) is about 1.5–4 times larger than e_h 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_h^* , $(Q_h^*)^2$ and k_h^* 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_h^* , e_h^* , $(Q_h^*)^2$, and k_h^* (Figs. 2 and 3) of the 2–0–2 composites examined here make them attractive for hydroacoustic and transducer applications.

Acknowledgements

The authors would like to thank Prof. Dr. A. A. Nesterov, Prof. Dr. V. P. Sakhnenko, Prof. Dr. I. A. Parinov (Southern Federal University, Russia), and Prof. Dr. S.-H. Chang (National Kaohsiung Marine University, Taiwan, ROC) for their interest in the research problem. The results on the research work No. 1597 have been represented within the framework of the base part of the state task No. 2014/174 in the scientific activity area at the Southern Federal University (Russia). Prof. Dr. C. R. Bowen acknowledges funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013) / ERC Grant Agreement no.320963 on Novel Energy Materials, Engineering Science and Integrated Systems (NEMESIS).

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