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# New aspect-ratio effect in three-component composites for piezoelectric sensor, hydrophone and energy-harvesting applications

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ABSTRACT

In this paper the influence of the aspect ratio of ferroelectric ceramic inclusions on the piezoelectric performance and hydrostatic parameters of novel three-component 1–3-type composites based on relaxor-ferroelectric single crystals is studied. Differences in the microgeometry of the ceramic/polymer matrix with 0–3 connectivity and the presence of two piezo-active components with contrasting piezoelectric and mechanical properties lead to a considerable dependence of the piezoelectric performance, hydrostatic response and related parameters of the 1–0–3 composite on the aspect ratio and volume fraction of the aligned ceramic inclusions. The influence of the elastic anisotropy of the ceramic/polymer matrix on composite properties with changes in the aspect ratio and volume fraction of the inclusions is discussed. The piezoelectric performance of the 1–0–3 $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.33PbTiO_3$ single crystal/modified $PbTiO_3$ ceramic/polymer composite suggests that such a material is of interest for both sensor and energy-harvesting applications due to large values of the piezoelectric coefficient $g^*_{33} \approx 400-550$ mV m/N, squared figure of merit $d^*_{33}g^*_{33} \sim 10^{-10}$ Pa$^{-1}$ and related anisotropy factor $d^*_{33}g^*_{33}/(d^*_{31}g^*_{31}) \approx 8-9$. Such composites can also be used in hydrophone applications due to their large hydrostatic parameters, e.g., $d^*_h \sim 10^2$ pC/N, $g^*_h \approx 100-160$ mV m/N and $d^*_h g^*_h \sim 10^{-11}$ Pa$^{-1}$.



## 1. Introduction

There is a continued interest in advanced piezo-active composites based on relaxor-ferroelectric single crystals (SCs) [1–4] as a result of the high piezoelectric activity of the SC component [5–8] and polarisation orientation effects [3]. This makes such composites attractive for a variety of important piezotechnical applications, such as sensing and energy harvesting [9]. Of particular interest are relaxor-ferroelectric SC/polymer composites [1–3] with 1–3 connectivity in terms of the work of Newnham et al. [10]. SCs of perovskite-type relaxor-ferroelectric solid solutions of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ (PMN − xPT) and $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ with engineered domain structures [5,6,8] exhibit high piezoelectric coefficients $d_{3j} \sim 10^3$ pC/N (see, e.g., Table 1), large electromechanical coupling factors $k_{3j}$ etc. and are therefore strong candidates as highly effective components for modern 1–3 composites [1,2]. A 1–3 composite architecture, which consists of a system of long parallel SC rods in a continuous polymer matrix, can be further modified by the formation of either pores or a system of inclusions in the polymer matrix [11–13]. This additional approach to varying the composite architecture opens up a variety of new methods to tailor the electromechanical coupling, piezoelectric and other characteristics of this composite.

The stimulus for this study of composites based on relaxor-ferroelectric SC is to examine the ability to tailor the effective electromechanical properties of the heterogeneous matrix [12,13] and to optimise specific parameters of the composite [11]. In our opinion, the potential of further improvements of the piezocomposite performance is associated with the influence of the aspect ratio of the inclusions within the two-component matrix on the effective electromechanical properties of a three-component composite. Earlier work has studied the *aspect-ratio effect* in 1–3 [14,15], 2–2 [16] and 0–3 [17] composites based on ferroelectric ceramics (FCs). In these simple two-component composites the geometric sizes of FC rods (1–3 connectivity) relative to the size of the surrounding polymer matrix, geometric sizes of the FC and polymer layers (2–2 connectivity) and ratios of semi-axes of spheroidal FC inclusions (0–3 connectivity) were varied. However, to the best of our knowledge, no publication has examined the aspect-ratio effect in three-component composites that contain

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relaxor-ferroelectric SC, FC and polymer, i.e., three kinds of components that are suitable for the manufacture of advanced piezo-composites. The aim of the present paper is to describe and provide a detailed analysis of a *new aspect-ratio inclusion effect* in 1–3-type composites, wherein a 0–3 FC/polymer matrix with variable properties plays an important role in tailoring the composite properties, and to show the performance of this composite in the context of specific piezotechnical applications such as sensors, hydrophones and energy harvesting.

## 2. Model concept and effective parameters

It is assumed that the three-component composite consists of long relaxor-ferroelectric SC rods embedded in a FC/polymer matrix (Fig. 1a). The SC rods are in the form of a rectangular parallelepiped with square cross sections in the $(X_1OX_2)$ plane, whose centres are arranged into a square array (Fig. 1b). The spontaneous polarisation of each rod is characterised by $\boldsymbol{P_s}^{(1)} || OX_3$. The main crystallographic axes of each rod are oriented as follows: X$||OX_1$, Y$||OX_2$ and Z$||OX_3$. The shape of each FC inclusion in the FC/polymer matrix (see inset in Fig. 1a) 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 rectangular co-ordinate system $(X_1X_2X_3)$, where $a_1$, $a_2 = a_1$ and $a_3$ are

**Table 1**
Room-temperature elastic compliances $s_{ab}^E$ (in $10^{-12}$ Pa$^{-1}$), piezoelectric coefficients $d_{fl}$ (in pC/N) and relative dielectric permittivities $\varepsilon_{rr}^{\sigma}/\varepsilon_0$ of [001]-poled domain-engineered PMN–0.33PT SC (4 mm symmetry) [5].

| $s_{11}^E$ | $s_{12}^E$ | $s_{13}^E$ | $s_{33}^E$ | $s_{44}^E$ | $s_{66}^E$ | $d_{31}$ | $d_{33}$ | $d_{15}$ | $\varepsilon_{11}^{\sigma}/\varepsilon_0$ | $\varepsilon_{33}^{\sigma}/\varepsilon_0$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 69.0 | −11.1 | −55.7 | 119.6 | 14.5 | 15.2 | −1330 | 2820 | 146 | 1600 | 8200 |

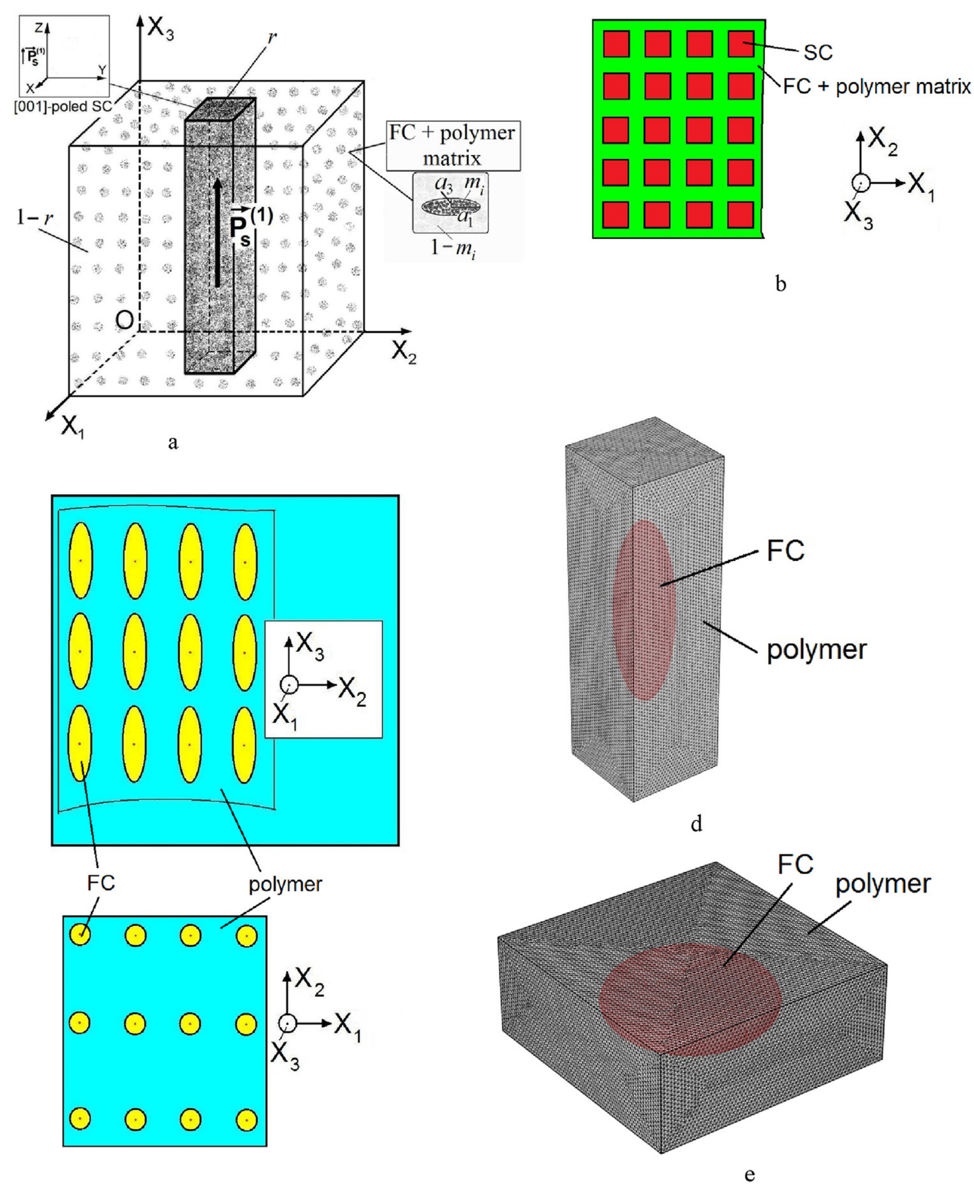


**Fig. 1.** Schematic of the 1–0–3 relaxor-ferroelectric SC/FC/polymer composite (a), the arrangement of SC rods with square bases in a surrounding medium (b), the arrangement of spheroidal FC inclusions in a polymer matrix (c), and meshes of the 0–3 composite matrix at $0 < \rho_i < 1$ (d, for finite element modelling) and at $\rho_i > 1$ (e, for finite element modelling). (a)–(c) $(X_1X_2X_3)$ is a rectangular co-ordinate system concerned with the composite sample. $\boldsymbol{P_s}^{(1)}$ is the spontaneous polarisation of the SC rod, $r$ and $1 - r$ are volume fractions of the SC rods and the surrounding 0–3 matrix, respectively, $m_i$ is the volume fraction of the isolated FC inclusions in the polymer medium, and $a_1$ and $a_3$ are semi-axes of each FC inclusion.