

PIEZOELECTRIC RESPONSE OF POROUS CERAMIC AND COMPOSITE MATERIALS BASED ON $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$: EXPERIMENT AND MODELLING

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Abstract

This paper presents experimental and theoretical studies of the effective piezoelectric properties of porous $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ -based ceramics and composites. Experimental dependences of piezoelectric coefficients, dielectric permittivity and figures of merit on relative density are determined for porous materials containing different piezopassive components. The features of the piezoelectric response of these materials in a wide range of volume concentration of the piezopassive components are analysed using a model consisting of a laminated composite with 2-2 and 1-3 connectivity elements. The role of these elements in forming different concentration dependences of the effective parameters of the porous piezoceramic and piezocomposite materials is discussed.

keywords: composites, porosity, dielectric properties, ferroelectric properties.

Introduction

Porous ceramics and composites based on ferroelectric $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ perovskite-type solid solutions are important examples of piezoactive materials that have been intensively studied in the last decades as potential materials for hydrophone and piezotechnical applications [1-3]. The porous ceramics and composites offer considerable improvements over monolithic ceramics due to large values of effective parameters, such as hydrostatic piezoelectric coefficients $d_h^* = d_{33}^* + 2d_{31}^*$ and $g_h^* = g_{33}^* + 2g_{31}^*$ [1,3], piezoelectric coefficients d_{33}^* and g_{33}^* [2,4], electromechanical coupling factors k_{33}^* and k_t^* [2], squared figures of merits $(Q_{33}^*)^2 = d_{33}^*g_{33}^*$ and $(Q_h^*)^2 = d_h^*g_h^*$ [4], etc.

To our best knowledge, studies of microstructures of porous piezoactive ceramic and composite materials have been carried out by only a few researchers [3,4,5,6]. Many processing routes result in microstructures containing closed pores or open pores that are described by 3-0 or 3-3 connectivity, respectively, in the terminology by Newnham et al. [7]. In some cases, mixtures of isolated and interconnected pores are also observed. For the analysis of the effective piezoelectric, dielectric, elastic, and other properties of these materials, different micromechanical models [6,4,8-10] have been presented. However, apart from [10], the existing theoretical approaches do not enable modelling of the microstructure–property relationships for both 3-0 and 3-3 connectivities. This approach stimulates a search for new possibilities of characterisation of microstructures and for microstructural elements influencing physical properties. In the present work we present experimental data on porous $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ -based ceramics and composites and attempt to describe features of piezoelectric response of these materials in the framework of a model consisting of a laminated composite with 2-2 and 1-3 connectivity elements from reference [11].

Properties of porous materials (experimental results)

Figs. 1-5 presents typical properties of porous piezoelectric materials (PZT-air) and polymer impregnated ceramic foams (PZT-polymer). Precise processing details and measurement methods are presented in other papers [12,13]. In brief, the low-density piezoelectric foams (<0.3 relative density) were prepared by coating polymeric foams with a ceramic suspension

and sintering. The higher density materials (>0.3 relative density) were fabricated using a variety of volatile additives added to Pb(Zr,Ti)O₃ powder before uniaxial pressing. The additives used were polyethylene oxide (PEO), Perspex (PMMA), corn flour (CR) and self-raising flour (SR). The additive produced porosity within the ceramics by volatilisation during heat treatment. In all cases PZT-5H was used as the ceramic component and all results are normalised with respect to the properties of the dense material.

Fig. 1 shows d_{33}^* against relative density for foams and different volatile additives. The general trend is a decrease in the value of d_{33}^* with decreasing relative density. It can be seen that different production methods produce different d_{33}^* values for the same relative density. Variations between additives are related to the different porous structures that are formed within the material [12]. The variation of d_{31}^* with relative density is shown in Fig.2. The absolute value of d_{31}^* decreases with decreasing relative density; but at a more rapid rate compared to d_{33}^* . The rapid decrease in d_{31}^* and subsequent increase in piezoelectric anisotropy (d_{33}^*/d_{31}^*) results in high d_h^* values, as observed in Fig. 3. A maximum d_h^* is present at 0.5-0.75 relative density. The highest values of d_h^* are obtained using PMMA as the inclusion material. The foam based materials, while resulting in a modest value of d_h^* (100–200pCN⁻¹), still show a higher value than for dense PZT-5H (~50pCN⁻¹). These foam materials have many other material property advantages, such as low density and acoustic impedance in their favour.

Fig. 4 shows the normalised relative permittivity against relative density revealing that permittivity decreases with decreasing density. The samples made with PMMA however have the lowest values of permittivity for a specific density. This is explained by cracking observed in these samples perpendicular to the poling direction [12] reducing the amount of material that has an uninterrupted path from the top to the bottom of the sample. The CS samples have a higher permittivity, possibly due to the very small pores and a large amount of the bulk material is left continuous. The g_h^* ($=d_h^*/\epsilon_{33}^{*T}$) data are presented in fig. 5. PMMA samples have high values of g_h^* due to their suppressed values of ϵ_{33}^{*T} and d_{31}^* caused by the cracking of samples during manufacture. It can also be seen that the CS samples have a lower value of g_h^* than the PEO and SR samples, due to the high permittivity values of the CS samples. PZT-air foam based materials exhibit high g_h^* but

are difficult to use due to their poor mechanical strength, however the PZT-polymer foam based materials, while having a lower value of g_h are robust and well suited to applications such as hydrophones.

Properties of porous material (model results)

In our opinion, the considerable increase in the piezoelectric anisotropy (d_{33}^*/d_{31}^*) and rapidly decreasing d_{31}^* on increasing the porosity or volume concentration of the piezopassive components m_p (polymer or air) are due to the presence of elements of the structure with 2-2 connectivity, i.e., layers of piezoceramic. An example of the structure of the modified laminated composite has been considered in paper [10]. Based on these results, we put forward a model which represents an interconnected composite that contains two types of piezoactive layers (Fig. 6). According to this model, the layer of the first type represents a piezopassive matrix reinforced by a system of piezoceramic cylindrical rods being lengthy and parallel to the poling axis OX_3 (1-3 connectivity). The layer of the second type is assumed to be piezoceramic and lengthy in both OX_1 and OX_2 directions (2-2 connectivity). These layers, which alternate along the OX_3 direction, are the main elements of the structure of porous ceramic or composite materials. Their remanent polarization vectors $\mathbf{P}_{R,i}$ are assumed to be oriented perpendicular to interfaces.

The observed slight decrease of d_{33}^* at increasing m_p is provided owing to a continuous distribution of the piezoceramic framework along the poling axis OX_3 , and it can take place at the presence of elements of the structure with 1-3 connectivity. Volume concentrations of their piezoactive (m_{act}) and piezopassive (m_p) components can be determined from Fig. 6. If m_r and $1-m_r$ are volume concentrations of the piezoceramic rods and the surrounding piezopassive matrix (polymer or air), respectively, m_s is the volume concentration of the layers containing the above-mentioned piezoceramic rods then $m_{act} = m_s m_r + 1 - m_s$ and $m_p = m_s(1 - m_r)$.

Effective electromechanical constants x^* of the porous material are calculated by using formulas for two-component piezoactive composites in two stages. Averaging m_r follows formulas [14] (1-3 connectivity) and averaging on m_s is enabled using formulas [15] (2-2 connectivity). For calculations, room-temperature experimental electromechanical constants

of following components were used: poled ferroelectric ceramic PZT-5H [9], polyethylene [10] and elastomer [14]. Examples of concentration behaviour of normalized effective parameters of porous PZT-5H based materials are shown in Table 1, where the superscript (PZT-5H) denotes the dense ceramic.

The calculated parameters can be compared in two ways. First, the comparison of effective parameters x^* or ratios $x^* / x^{(PZT-5H)}$ in cases I and II in Table 1 enable us to conclude as follows. The substitution of polyethylene by more compliant polymer (an elastomer) results in increasing dielectric permittivity $\epsilon_{33}^{*T}(m_s, m_r)$ and piezoelectric coefficients $d_{3j}^*(m_s, m_r)$, $d_h^*(m_s, m_r)$ and $g_h^*(m_s, m_r)$ at fixed concentration parameters m_s and m_r . This substitution influences the piezoelectric anisotropy $d_{33}^*(m_s, m_r) / d_{31}^*(m_s, m_r)$ mainly due to the change in the ratio $c_{11}^{(p)} / c_{12}^{(p)}$ of elastic moduli of polymer.

Second, as we compare data from cases II and III, one can conclude that the changes in $\epsilon_{33}^{*T}(m_s, m_r)$ and $d_{31}^*(m_s, m_r)$ are relatively small. However, values of $d_{33}^*(m_s, m_r)$, $d_h^*(m_s, m_r)$ and $g_h^*(m_s, m_r)$ increase by substituting the monolithic elastomer matrix by air. In our opinion, such behaviour is accounted for the weak electromechanical interaction between piezoceramic rods in the OX_1 and OX_2 directions (due to the presence of the piezopassive matrix). As is known from earlier work [14] on 1-3 piezoactive composites, softening the matrix surrounding the piezoelectric rods provides more high values of the effective piezoelectric coefficients d_{33}^* , g_{33}^* , d_h^* , and g_h^* even at small volume concentrations of the rods. In addition, an important consequence of slight concentration dependence $d_{33}^*(m_s, m_r)$ in cases II and III from Table 1 consists in an equality $g_{33}^* / g_{33}^{(PZT-5H)} = (Q_{33}^*)^2 / (Q_{33}^{(PZT-5H)})^2$ that holds true with accuracy up to a few percents.

A comparison of experimental results (Figs.1-5) and predicted values (Table 1) shows agreement of concentration dependences are observed in a wide m_p and m_s range. As m_p increases, the concentration parameter m_s also increases, i.e. $m'_s > m_s$ at $m'_p > m_p$. It is remarkable to note that a relation $m'_p / m_p \approx m'_s / m_s$ remains correct at $0.10 < m_p < 0.60$. As the polymer concentration (m_p) approaches 0.60, a comparison of experimental and calculated parameters becomes problematic. These parameters would be in good agreement at $m_r < 0.10$, however the structure of the porous composite with very small m_r values at $m_s > 2/3$ becomes unstable and could be destroyed even a small mechanical loading.

Apparently, this fact emphasizes the upper bound of volume concentration $m_p = 0.60$ for the range where the proposed model can be used for interpretation of experimental data. In summary, a model of a modified laminated composite with 2-2 and 1-3 connectivity elements has enabled some of the features of microstructure-property relationships in porous ceramics and composites with mixed connectivities to be described.

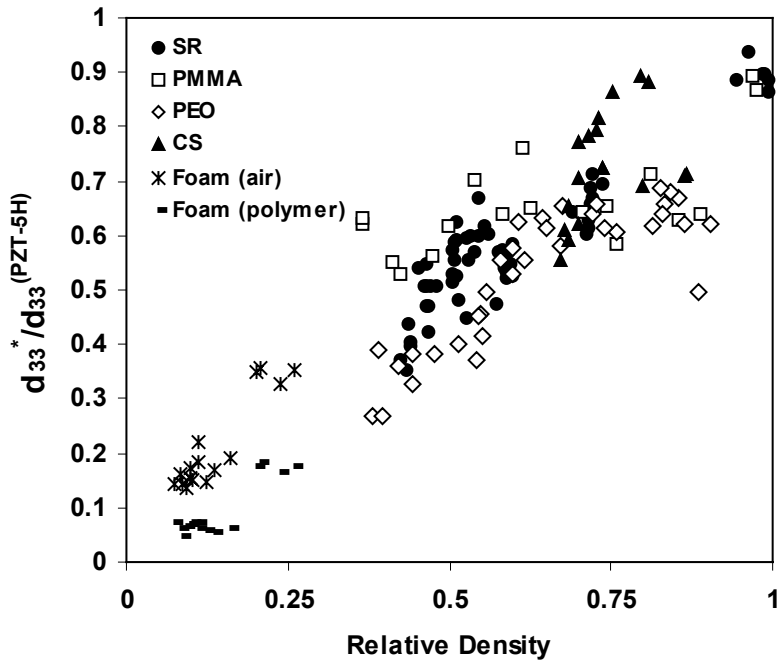


Figure 1: $d_{33}^* / d_{33}^{(PZT-5H)}$ vs. relative density

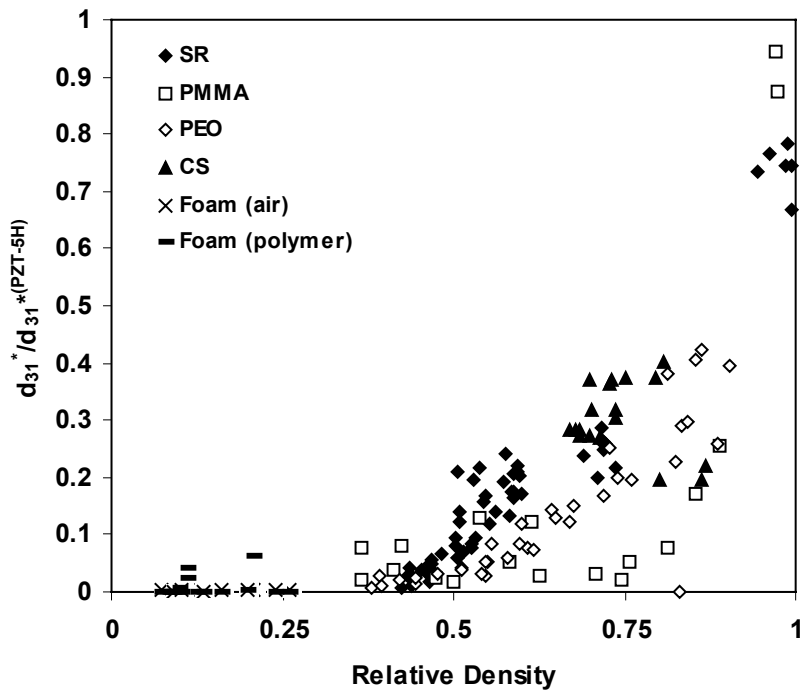


Figure 2: $d_{31}^* / d_{31}^{(PZT-5H)}$ vs. relative density

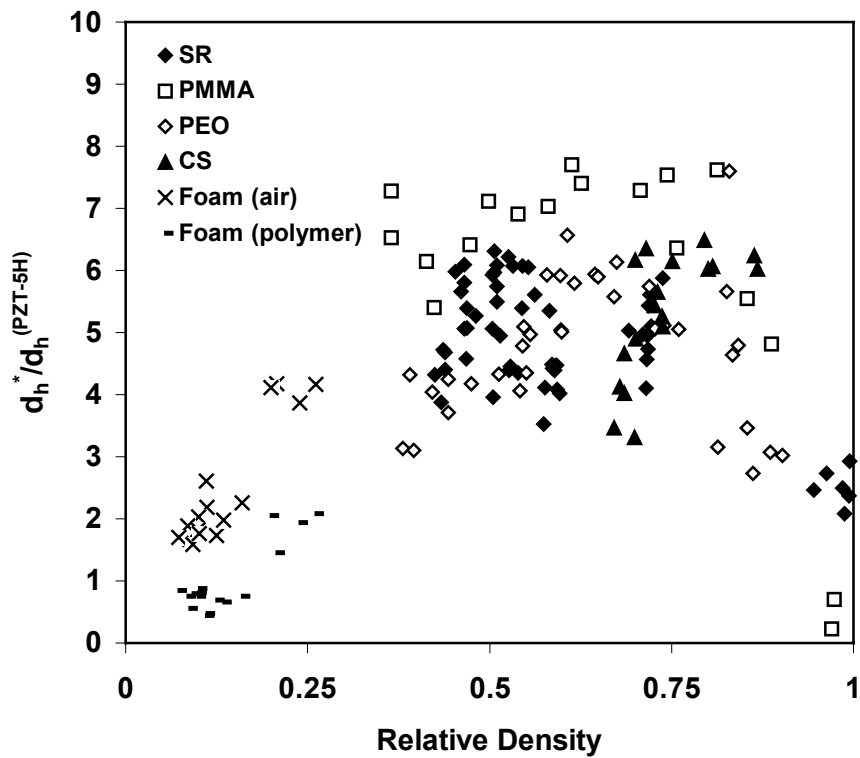


Figure 3: $d_h^*/d_h^{(PZT-5H)}$ vs. relative density. d_h^* calculated from $d_h^* = d_{33}^* + 2d_{31}^*$.

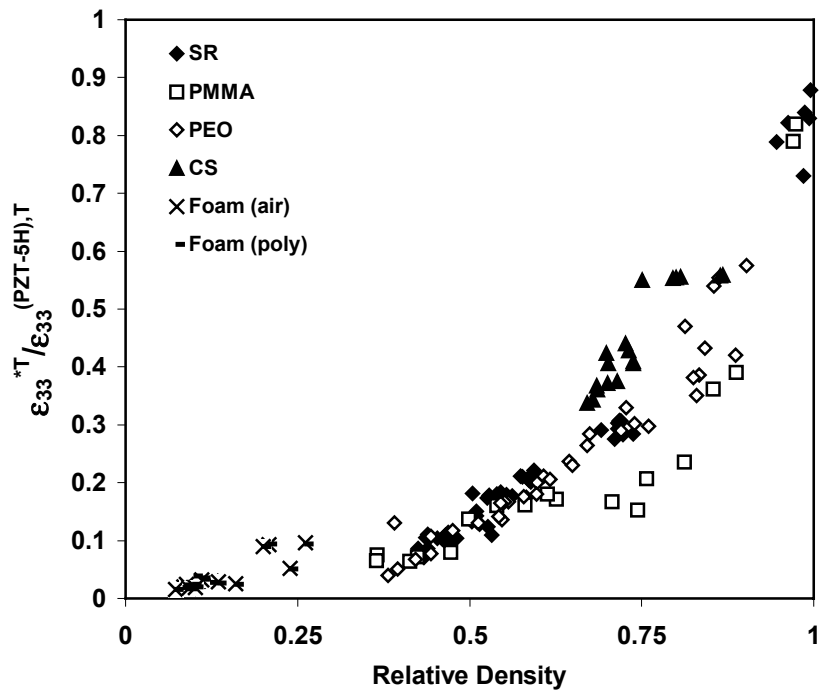


Figure 4: $\epsilon_{33}^*/\epsilon_{33}^{(PZT-5H),T}$ vs. relative density.

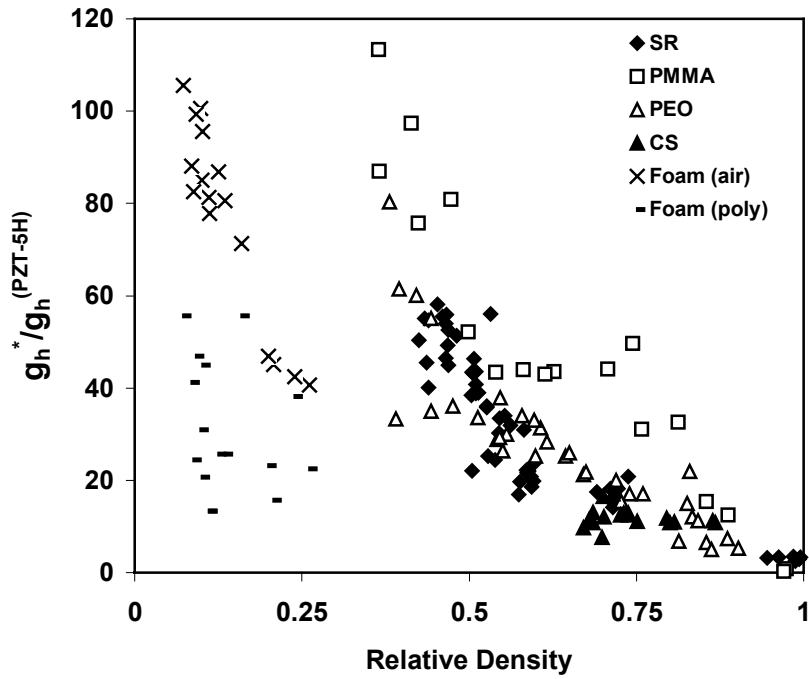


Figure 5: $g_h^*/g_h^{(PZT-5H)}$ vs. relative density.

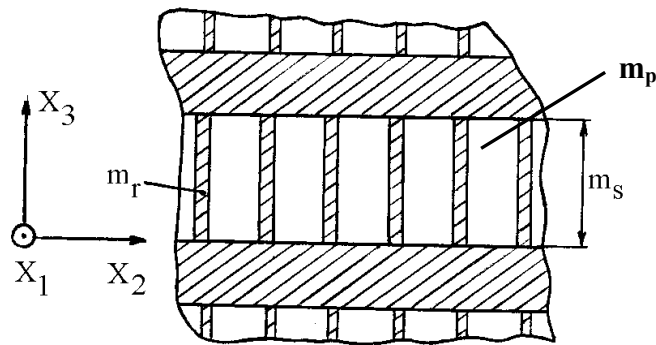


Figure 6. Schematic diagram showing the structure of the porous piezoelectric ceramic or the porous composite on the basis of the piezoelectric ceramic. Dashed area is the monolithic ceramic component. m_{act} is the volume concentration of the piezoelectric phase. m_p is the volume concentration of the polymer phase. OX_3 is the poling direction

Table 1. Calculated ratios of parameters $x^* / x^{(PZT-5H)}$ of composite materials based on PZT-5H

m_s	m_r	$m_p = m_s(1 - m_r)$	$\epsilon_{33}^{*T} / \epsilon_{33}^{(PZT-5H),T}$	$d_{31}^* / d_{31}^{(PZT-5H)}$	$d_{33}^* / d_{33}^{(PZT-5H)}$	$d_h^* / d_h^{(PZT-5H)}$	$g_h^* / g_h^{(PZT-5H)}$
Case I: PZT-5H - polyethylene							
0.10	0.08	0.092	0.40	0.41	0.72	2.68	6.76
0.20	0.10	0.180	0.30	0.33	0.72	3.20	10.5
0.30	0.12	0.264	0.27	0.30	0.74	3.51	13.0
0.40	0.10	0.360	0.18	0.22	0.67	3.56	19.8
0.50	0.09	0.455	0.13	0.18	0.63	3.53	26.5
0.60	0.05	0.570	0.06	0.10	0.47	2.80	48.0
0.65	0.04	0.624	0.04	0.08	0.40	2.47	59.1
Case II PZT-5H - elastomer							
0.10	0.08	0.092	0.44	0.45	0.87	3.61	8.26
0.20	0.10	0.180	0.33	0.35	0.87	4.26	12.7
0.30	0.12	0.264	0.30	0.31	0.88	4.58	15.6
0.40	0.10	0.360	0.20	0.22	0.85	4.91	24.4
0.50	0.09	0.455	0.15	0.17	0.82	5.05	33.4
0.60	0.05	0.570	0.07	0.10	0.70	4.69	67.2
0.65	0.04	0.624	0.05	0.07	0.65	4.42	86.9
Case III: PZT-5H - air							
0.10	0.08	0.092	0.47	0.47	1	4.37	9.38
0.20	0.10	0.180	0.36	0.36	1	5.05	14.1
0.30	0.12	0.264	0.31	0.31	1	5.34	17.0
0.40	0.10	0.360	0.22	0.22	1	5.94	27.2
0.50	0.09	0.455	0.17	0.17	1	6.27	37.8
0.60	0.05	0.570	0.08	0.08	1	6.80	83.9
0.65	0.04	0.624	0.06	0.06	1	6.93	114

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