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Calculation of the Piezomoduli of Depolarized Piezoceramics

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Abstract

The piezoelectric constants of d^*_{ik} *electrically depolarized (remanent polarization* $P=0$*) piezoceramics are calculated from the constants of single-domain crystallite with the aid of the effective medium approximation. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

The possibility of the existence of ferroelectric ceramic piezoelectrics of polar groups of symmetry and not possessing macroscopic polarization was substantiated in previous papers.[1,2] Such piezoelectrics as well as crystals of acentric (noncentrosymmetric) nonpolar classes do not exhibit effects linked with the macroscopic polarization (pyroeffect, piezoeffect produced by hydrostatic pressure) and in this respect may be named nonpolar. Depolarized piezoceramics with zero remanent polarization ($P=0$) are also examples of nonpolar piezoelectrics.

In this work we have calculated the piezomoduli d^*_{ik} (and also dielectric constants ε^{*T}_{kk} and elastic compliance coefficients s^{*E}_{ik}) of ferroceramics from the constants of single-domain crystallite at the arbitrary poling field with the aid of the effective medium approximation.[3]

2 Mathematical Development

Let us assume that the polarized state in the sample is caused by 180° reorientations. The relations between the internal electrical field (mechanical stress) in a spherical monodomain crystallite and the electrical field (mechanical stress) in the surrounding ceramic matrix (which is assumed to be isotropic) are determined by the equations.[3] To carry out the calculation, let us transform these equations to the following equivalent form:

$$
\begin{aligned}
&(\eta^S_{11}+\alpha)D_1 - h_{15}S_5 = E^0_1 + \alpha D^0_1,\\
&(\eta^S_{11}+\alpha)D_2 - h_{15}S_4 = E^0_2 + \alpha D^0_2,\\
&(\eta^S_{33}+\alpha)D_3 - h_{31}S_1 - h_{31}S_2 - h_{33}S_3 = E^0_3 + \alpha D^0_3,\\
&(c^D_{11}+\beta_1)S_1 + (c^D_{12}+\beta_2)S_2 + (c^D_{13}+\beta_2)\\
&\quad\times S_3 - h_{31}D_3 = T^0_1 + \beta_1 S^0_1 + \beta_2 S^0_2 + \beta_2 S^0_3,\\
&(c^D_{12}+\beta_2)S_1 + (c^D_{11}+\beta_1)S_2 + (c^D_{13}+\beta_2)\\
&\quad\times S_3 - h_{31}D_3 = T^0_2 + \beta_2 S^0_1 + \beta_1 S^0_2 + \beta_2 S^0_3,\\
&(c^D_{13}+\beta_2)S_1 + (c^D_{13}+\beta_2)S_2 + (c^D_{33}+\beta_1)\\
&\quad\times S_3 - h_{33}D_3 = T^0_3 + \beta_2 S^0_1 + \beta_2 S^0_2 + \beta_1 S^0_3,\\
&(c^D_{44}+\beta_4)S_4 - h_{15}D_2 = T^0_4 + \beta_4 S^0_4,\\
&(c^D_{44}+\beta_4)S_5 - h_{15}D_1 = T^0_5 + \beta_4 S^0_5,\\
&(c^D_{66}+\beta_4)S_6 = T^0_6 + \beta_4 S^0_6,
\end{aligned}
\tag{1}
$$

where h_{ij}, η^S_{ki}, c^D_{ij} are the crystallite piezoelectric-stress constants, dielectric impermeability at constant strain and elastic stiffness at constant electric displacement; E_k, D_k, T_k, S_k, E^0_k, D^0_k, T^0_k, S^0_k, are the electric field, the electric displacement, the mechanical stress and the mechanical strain inside and outside the crystallite, respectively; α is the depolarising factor; β is the destressing factor. The factors (describing the crystallite interaction) α and β can be represented in following form:

$$
\begin{aligned}
\alpha &= \frac{1}{2\varepsilon*},\\
\beta_1 &= \frac{5\left(s^*_{11}+s^*_{12}\right)}{s^*_{12}s^*_{11} - 5s^{*2}_{12} + 4s^{*2}_{11}},\\
\beta_2 &= \frac{3s^*_{11}+5s^*_{12}}{2\left(s^*_{12}s^*_{11} - 5s^{*2}_{12} + 4s^{*2}_{11}\right)},\\
\beta_4 &= \frac{1}{2}(\beta_1 - \beta_2)
\end{aligned}
\tag{2}
$$

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where ε^* is the dielectric permittivity, and s^*_{11}, s^*_{12} are the elastic compliance coefficients of unpolarized ceramics. The system of linear eqn (1) in the variables D_k, S_k has the symmetric matrix. Let us denote this matrix by Δ. The components Δ_{ik} can be written as:

$$\begin{aligned}
&\Delta_{11} = \Delta_{22} = \eta^S_{11} + \alpha,\, \Delta_{33} = \eta^S_{33} + \alpha,\\
&\Delta_{18} = \Delta_{27} = -h_{15},\, \Delta_{34} = \Delta_{35} = -h_{31},\\
&\Delta_{36} = -h_{33},\, \Delta_{44} = \Delta_{55} = c^D_{11} + \beta_1,\\
&\Delta_{45} = c^D_{12} + \beta_2,\, \Delta_{46} = \Delta_{56} = c^D_{13} + \beta_2,\\
&\Delta_{66} = c^D_{33} + \beta_1,\, \Delta_{77} = \Delta_{88} = c^D_{44} + \beta_4,\\
&\Delta_{99} = c^D_{66} + \beta_4
\end{aligned} \tag{3}$$

The other components of the matrix Δ are equal to zero. From the system (1) D_k, S_k can be solved as functions $E^0{}_k$, $S^0{}_k$, $D^0{}_k$ and $T^0{}_k$. Then, transforming components D_k and S_k to the ceramics coordinate system and averaging them over orientations, we obtain the system of the equations for the ceramics material constants d^*_{ik}, ε^{*T}_{kk} and s^{*E}_{ij}

$$\begin{aligned}
&\varepsilon^{*T}_{11} = \mu\left(1 + \alpha\varepsilon^{*T}_{11}\right) + \frac{3}{4}\lambda_{31}\beta_1(1-b)d^*_{15},\\
&\varepsilon^{*T}_{33} = \mu\left(1 + \alpha\varepsilon^{*T}_{33}\right) + \beta_1[(3b-1)\lambda_{31} + \lambda_{33}]d^*_{33}\\
&\quad + \beta_1[(3b+1)\lambda_{31} + (3b-1)\lambda_{33} + \lambda_{33}]d^*_{31},\\
&d^*_{31} = \lambda_{31}\left(1 + \alpha\varepsilon^{*T}_{33}\right) + \left(2d^*_{33} + 3d^*_{31}\right)b - d^*_{33} - d^*_{31},\\
&d^*_{33} = \lambda_{33}\left(1 + \alpha\varepsilon^{*T}_{33}\right) + \left(d^*_{33} + 4d^*_{31}\right)b - 2d^*_{31},\\
&d^*_{15} = \lambda_{15}\left(1 + \alpha\varepsilon^{*T}_{11}\right) + (1-b)d^*_{15},\\
&s^{*E}_{11} = \lambda_{31}\alpha d^*_{31} + \left(2s^{*E}_{12} + 2s^{*E}_{13} + s^{*E}_{11}\right)b - s^{*E}_{13} - s^{*E}_{12} + s_1,\\
&s^{*E}_{33} = \lambda_{33}\alpha d^*_{33} + \left(4s^{*E}_{13} + s^{*E}_{33}\right)b - 2s^{*E}_{13} + s_1,\\
&s^{*E}_{12} = \lambda_{31}\alpha d^*_{31} + \left(2s^{*E}_{12} + 2s^{*E}_{13} + s^{*E}_{12}\right)b - s^{*E}_{13} - s^{*E}_{11} + s_2,\\
&s^{*E}_{13} = \lambda_{31}\alpha d^*_{33} + \left(3s^{*E}_{13} + 2s^{*E}_{33}\right)b - s^{*E}_{13} - s^{*E}_{33} + s_2,\\
&s^{*E}_{55} = \lambda_{15}\alpha d^*_{15} + (1-b)s^{*E}_{55} + s_4,
\end{aligned} \tag{4}$$

in which the following notations used:

$$\begin{aligned}
&b = \frac{1}{3} + \frac{2\beta_2}{3\beta_1},\, S_1 = \frac{\beta_1 + 6\beta_2}{3\beta_1(\beta_1 + 2\beta_2)},\\
&S_2 = \frac{2\beta_2 - \beta_1}{3\beta_1(\beta_1 + 2\beta_2)},\, S_4 = \frac{4}{3\beta_1}
\end{aligned} \tag{5}$$

If R is the matrix inverse of Δ, then for depolarized piezoceramics with zero remanent polarization $P = P_s\langle\cos\theta\rangle = 0$ (P_s is the spontaneous polarization) the coefficients μ, λ_{33}, λ_{31}, and λ_{15} in the eqn (4) are expressed in terms of R_{ik} as

$$\begin{aligned}
&\mu = \frac{1}{3}(R_{11} + R_{22} + R_{33}),\\
&\lambda_{33} = \frac{1}{2}(2R_{36} - R_{27} - R_{34} - R_{18} - R_{35})\langle\cos^3\theta\rangle,\\
&\lambda_{31} = -\frac{1}{2}\lambda_{33},\, \lambda_{15} = -\lambda_{33},
\end{aligned} \tag{6}$$

where the angle θ is the angle between the direction of the spontaneous polarization of a crystallite and the direction of the field applied for poling the ceramics. The angular brackets mean that the corresponding expressions are averaged over the various orientations.

The tensor d^*_{ik} can be calculated by analytical solution of (4). This solution can be written as

$$\begin{aligned}
&d^*_{33} = -2d^*_{31} = \frac{12\lambda_{33}}{27\alpha\beta_1(b-1)\lambda^2_{33} + 8b},\\
&d^*_{15} = -\frac{12\lambda_{33}}{9\alpha\beta_1,\,(b-1)\lambda^2_{33} + 8b}
\end{aligned} \tag{7}$$

The series expansion of the expressions (7), with respect to the variable λ_{33} (about the point $\lambda_{33}=0$, up to order 3) yields

$$\begin{aligned}
d^*_{33} = -2d^*_{31} = -d^*_{15} &= \frac{3}{2b}\lambda_{33}\\
&= \frac{9}{4}\beta_1\left(s^*_{11} - s^*_{12}\right)\lambda_{33}
\end{aligned} \tag{8}$$

For the dielectric and elastic constants by the series expansion of the solutions (4) we obtain the following expressions:

$$\begin{aligned}
&\varepsilon^{*T}_{11} = \varepsilon^* + \frac{3}{4}\beta_1 b(1-b)d^{*2}_{15},\\
&\varepsilon^{*T}_{33} = \varepsilon^* + \frac{9}{4}\beta_1 b(1-b)d^{*2}_{33},\\
&s^{*E}_{11} = s^*_{11} + \frac{2\alpha}{3}d^{*2}_{31},\, s^{*E}_{33} = s^*_{11} + \frac{2\alpha}{3}d^{*2}_{33},\\
&s^{*E}_{12} = s^*_{12} + \frac{2\alpha}{3}d^{*2}_{31},\, s^{*E}_{13} = s^*_{12} - \frac{\alpha}{3}d^{*2}_{31},\\
&s^{*E}_{55} = s^*_{44} + \frac{2\alpha}{3}d^{*2}_{15}
\end{aligned} \tag{9}$$

In eqn (9) the piezoelectric terms (the crystallite clamping effect) are usually much less than the constants of unpolarized ceramics. The anisotropy in depolarized piezoceramics is very small, and due to the crystallite (and domain) clamping effect. The crystallites and 180° domains in ferroelectric ceramics show similar behavior. The 'parallel' orientation of the crystallite polar axes produced by 180° -reversals remove the crystallite clamping effects.

The results of the calculations of physical constants of $BaTiO_3$ ceramics for monodomain (Calculation A) and polydomain (Calculation B) crystallite are shown in Table 1 together with our experimental results. As consistent with Ref.4 we considered (Calculation B) that the each crystallite in ceramics is split into 90° domains of two types having equal volume concentrations. The constants of polydomain crystallite were calculated by the method which was proposed in Ref.5.

Table 1. Dielectric, piezoelectric (d^*_{ik}, 10^{-12} m V^{-1}) and elastic (s^{*E}_{ik}, 10^{-12} m^2 N^{-1}) constants of electrically depolarized piezoceramics $BaTiO_3$ at 25°C

	$\varepsilon^T{}_{11}/\varepsilon_0$	$\varepsilon^T{}_{33}/\varepsilon_0$	d^*_{31}	d^*_{33}	d^*_{15}	s^{*E}_{11}	s^{*E}_{33}	s^{*E}_{12}	s^{*E}_{13}	s^{*E}_{55}
Calculation A	1310	1310	−12	24	−24	6·33	6·34	−2·23	−2·24	17·1
Calculation B	1020	1021	3·9	−7·8	7·7	6·56	6·56	−2·29	−2·29	17·7
Experiment	1360	1340	7	−14		8·5	9·0	−2·5	−2·7	

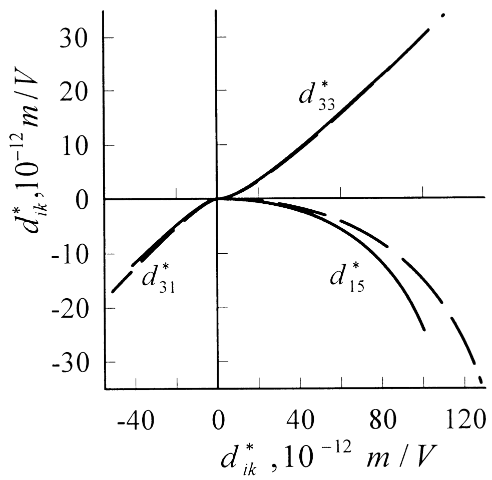

Fig. 1. Calculated relationships between the piezomoduli of polarized and depolarized ceramics $BaTiO_3$. The plot demonstrates that the calculated values with the aid of the effective medium approximation (solid curve) are in good agreement with calculated ones by averaging the components of the crystal piezomoduli tensor[7] (dotted curve).

As is seen from Table 1, the evaluations taking into account the domain structure of crystallite are in better agreement with the experiment.

The improved model[6] is also used here for calculation of the constants d^*_{ik} of depolarized ceramics. The results of these calculations are in agreement (error is less 1%) with the formulas (9). The piezoelectric constants can be calculated by using the method.[7] Fig. 1 shows the calculated values in comparison with the averaged values by the method[7] (dotted lines in Fig. 1). It is necessary to note that the agreement is enough good. The simplest approximation, namely averaging the crystal piezomoduli d_{ik} over the various orientations crystallites in the ceramics yields for the piezomodule of d^{*0}_{33} depolarized ceramics:

$$d^{*0}_{33} = \frac{1}{2} d^*_{33} - \frac{d_{33}\left(\sqrt{A} - d_{33}\right)}{4(d_{31} + d_{15} - d_{33})}, \qquad (10)$$
$$A = 4(d_{31} + d_{15} - d_{33}) d^*_{33} + d^2_{33}$$

This simple expression can be used for the estimate calculations.

3 Conclusions

Thus it is shown that the piezoelectric, dielectric and elastic constants of electrically depolarized ferroelectric ceramics can be calculated in satisfactory agreement with experimental values with the aid of a suitable averaging procedure. Exact agreement cannot be expected since properties of real ceramics are determined by some additional essential factors such as displacements of 90° domain walls, lattice defects etc. which have not been considered in the model calculation.

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