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Effective elastic properties for unpoled barium titanate

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Abstract

Piezoelectric devices with complex electrode geometries may contain regions of ferroelectric material that remain unpoled. It is desirable to account for these non-piezoelectric regions for device optimization, since the unpoled and poled material properties differ. The lack of published elastic properties for unpoled ferroelectrics, specifically the numerous commercial PZT compositions, reflects the difficulty of experimental measurement. In this work, a method was developed to predict unpoled properties from more commonly available poled material data. Barium titanate was chosen for study as a representative ferroelectric, with both single crystal and polycrystalline (ceramic) properties available. Finite element micro-mechanical models were created with a focus on computational economy. This allowed larger ensembles of results to be computed, providing accurate effective compliances when averaged. The modelling methodology predicted the elastic properties for unpoled barium titanate to within ~10% of measured experimental values.

Keywords: $BaTiO_3$ and titanates; Mechanical properties; Actuators; Sensors; Unpoled ferroelectrics

1. Introduction

Piezoelectric devices increasingly use complex electrode geometries for improved performance, as found in multilayer actuators,[1] active fibre composites[2] and emerging MEMS technology.[3] Such electrode arrangements can produce uneven electric field distributions to enhance actuation or lower driving voltages, but may also result in regions that experience little or no electric field. Where the electric field is lower than the coercive field ($<E_c$), the ferroelectric will remain unpoled. For device optimisation, it is desirable to account for the unpoled material that is not piezoelectric and possesses different permittivity and elastic constants to those of the poled state. For example, differences in the elastic constants can alter the frequency response of resonant devices or the blocking force achieved by an actuator.

Incorporating these factors into device design is hindered by the lack of published material data for unpoled ferroelectrics, specifically the range of commercial PZT compositions. PZT and barium titanate ceramics are isotropic in the unpoled state and characterised by a single permittivity (ε^0_{1r}) and two elastic constants such as Young's modulus (Y^0_{11}) and Poisson's ratio (ν^0_{12}), where superscript '0' denotes the unpoled condition. Experimental measurement of permittivity is achieved by capacitance readings, however, determining unpoled elastic properties is complex due to the time dependent, plastic ferroelastic contribution.[4] To minimise this effect it is necessary to adopt dynamic test methods, which require specialised experimental techniques.[4] The difficulty of these measurements has contributed to the lack of published material data. This may be resolved through calculating the effective elastic properties for an unpoled ferroelectric from poled (piezoelectric) material properties, measured by impedance analysis.

Devonshire[5] first considered that the bulk properties of polycrystalline barium titanate might be calculated by some directional average of the single crystal elastic constants. From this simple approach various improvements have been sought, first accounting for the inter-crystallite piezoelectric coupling,[6] to self-consistent effective medium methods,[7,8] to recent micro-mechanical finite element (FE) approaches.[9,10] However, the inherent weakness of these schemes is the requirement for single crystal data, which is not easily obtainable for many ferroelectrics, especially solid-solution materials such as PZT.

The aim of this study was to investigate whether the elastic properties of unpoled ferroelectrics could be predicted from the more commonly available poled *polycrystalline* data. To

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achieve this, a micro-mechanical FE model was developed. Barium titanate was selected as a representative ferroelectric that has been extensively studied[6,7,9,11,12] and unlike PZT, single crystal data is available for comparison.[11,13]

2. Method

2.1. Modelling approach

Approximating an unpoled ferroelectric by analytical[5–8,11] or FE methods[9,10] differ in technique, but tend to follow a common approach. A matrix of crystalline grains with an idealized microstructure is considered, where each grain has a random polarization (single domain) and appropriately orientated material properties. It is assumed that the bulk elastic response is a mixture of each grain's compliance with some piezoelectric and microstructural contribution. The resulting composite material should possess no overall polarization once averaged, being equivalent to an unpoled ferroelectric.

In designing the FE model for this study, the balance between accurately representing the material and computational economy was considered. In previous work the focus of FE modelling has been to replicate the material microstructure,[9,10] requiring high quality meshing with many elements. Due to this complexity, analysis has typically been limited to small representative volumes containing only a few grains. Further simplification is achieved by modelling in two-dimensions, although results from 2D plane strain or plane stress do not agree with comparable full 3D models.[9,10]

The approach adopted in this work was to depreciate the role of microstructure and develop an efficient three-dimensional model. This was based on the assumption that the elastic response is primarily governed by intrinsic atomistic factors. A simple cubic geometry was chosen that allowed each 'grain' to be represented by a single eight-node element, greatly improving the efficiency of model generation and solution times. Grain polarizations were quantized to just six orientations, corresponding to the two directions along the three principle axes.

The efficiency of this approach made larger three-dimensional models (up to 50,000 grains) practical, which were run in batches to examine a greater number of stochastic grain arrangements (~10,000 models). It was believed that averaging over a larger ensemble of different microstructures was beneficial compared to a limited sampling of more accurate microstructures.

2.2. Material properties

The accuracy of any analysis is limited by the quality of the data entered for the single-crystal material or poled piezoceramic. For this study, the elastic and piezoelectric coefficients were of primary concern as material inputs. These properties were validated by inversion of the elastic ($[s] \leftrightarrow [c]$) and piezoelectric ($[d] \leftrightarrow [e]$) matrices to highlight any inconsistencies (refer to footnote of Table 1). Where possible, the original or most accurately measured properties were used to generate the required material coefficients.

Table 1
Material properties for ceramic and single crystal barium titanate, presented in the form required for FE modelling with ANSYS

	Ceramic 1956[14]	Ceramic 1999[15]	Monocrystal 1958[11]	Monocrystal 1994[13]
c^E_{11} ($\times 10^9$ N m^{-2})	166[a]	158[b]	275[c]	222
c^E_{12} ($\times 10^9$ N m^{-2})	76.5[a]	69.1[b]	179[c]	108
c^E_{13} ($\times 10^9$ N m^{-2})	77.4[a]	67.5[b]	152[c]	111
c^E_{33} ($\times 10^9$ N m^{-2})	161[a]	150[b]	165[c]	151
c^E_{44} ($\times 10^9$ N m^{-2})	42.9[a]	45.1[b]	54.3[c]	61
c_{66} ($\times 10^9$ N m^{-2})	44.8[a]	44.6[b]	113[c]	134
ε^S_{1r}	1268	1000	1970	2200
ε^S_{3r}	1419	910	109	56
e_{31} (C m^{-2})	−4.38[a]	−3.14[b]	−2.69[c]	−1.03[d]
e_{33} (C m^{-2})	18.6[a]	14.5[b]	3.65[c]	6.18[d]
e_{15} (C m^{-2})	11.6[a]	10.9[b]	21.3[c]	34.4[d]
ρ (Mg m^{-3})	5.72	5.55	6.02	6.02

[a] Although c_{ij} and e_{ij} coefficients are presented by Bechmann,[14] these values were re-calculated from the measured s_{ij} and d_{ij} coefficients to ensure consistency (only minor variations were noted).

[b] Berlincourt et al.[15] provide c_{ij} and e_{ij} coefficients, but these were again re-calculated from the measured s_{ij} and d_{ij} coefficients. Disagreement was only noted for e_{33} (13.5 reported, 14.5 re-calculated). Note the material was a modified barium titanate.

[c] Values were calculated from the measured s_{ij} and d_{ij} coefficients from Berlincourt and Jaffe.[11]

[d] A disparity was found between the d_{ij} and e_{ij} coefficients reported by Zgonik et al.[13] Since d_{ij} values were experimentally measured and had greater accuracy, the e_{ij} coefficients were re-calculated.

Table 1 shows the properties for two poled barium titanate ceramics[14,15] and two single crystal materials.[11,13] This data was transformed into the six principle orientations by rotation of the matrices and assigned to each grain in the FE model, depending on the randomly allocated polarization.

2.3. Implementation

The model was implemented with the commercial FE code ANSYS 7.0, using an eight-node element capable of linear piezoelectric coupling ('SOLID5'). The elastic constants (Y^*_{11}, ν^*_{12}) were calculated by determining the strain in response to mechanical loading. Two electrical boundary conditions were investigated, since the stiffness of a poled ferroelectric varies depending on whether the material is 'closed circuit' ($\Delta E = 0$, voltage constrained on all faces) or 'open circuit' ($\Delta D = 0$, voltage is unconstrained). While these conditions affect the stiffness of a poled material, they should have no influence on an unpoled material.

For comparison uncoupled models were also investigated, with purely mechanical degrees of freedom as the FE code allowed the piezoelectric coupling to be deactivated for the chosen element type. The uncoupled results were validated against a simple rule of mixtures (RoM) average,[4] which assumes the domain polarizations are equally aligned in all three principle axes, such that:

$$Y^*_{11} = \frac{3}{s^{\mathrm{E}}_{11}} + \frac{3}{s^{\mathrm{E}}_{22}} + \frac{3}{s^{\mathrm{E}}_{33}} = \frac{3}{2s^{\mathrm{E}}_{11}} + \frac{3}{s^{\mathrm{E}}_{33}} \quad (1)$$

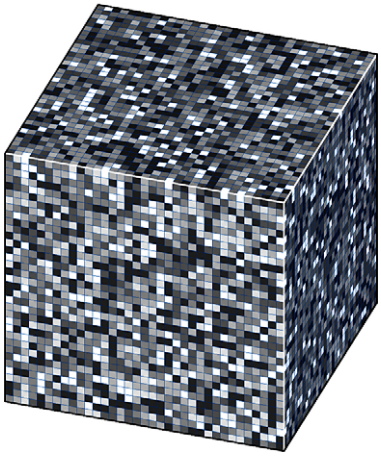

Fig. 1. A typical model with a fine microstructure (35 grains/side, $m \sim 0.029$). The shading of the elements corresponds to the six possible grain polarization directions.

where s_{11}^{E} $(= s_{22}^{E})$ and s_{33}^{E} are the constant field compliances perpendicular and parallel to the poling direction, respectively.

During development of the modelling technique, the influence of mesh density was considered. This parameter was represented by a relative mesh size (m), determined from the number of grain divisions (g) along one side of the model; hence, $m = 1/g$. It was found that while uncoupled models were not dependent on m, the coupled models were sensitive to the relative mesh size. It was therefore necessary to examine a range of mesh sizes for each material test case. For computational economy coarser meshing was preferred, with 6–35 grains per side. Fig. 1 shows a typical model with a fine microstructure, where $m = 1/35$. The model contains 42,875 (35^3) grains and ~1.4 million degrees of freedom.

3. Results and discussion

When plotting the elastic constant Y_{11}^{*} of the model (or equally ν_{12}^{*}, s_{11}^{*}, or s_{12}^{*}) as a function of relative mesh size m, a linear relationship was observed for all of the materials investigated. Fig. 2 shows the results from each individual model with a unique grain arrangement, at a particular mesh size, using either the polycrystalline (Fig. 2a) or single crystal (Fig. 2b) properties. Variation between individual models occurs due to the stochastic grain distributions, so it is necessary to run multiple models to find reliable averages. The polycrystalline (ceramic) materials with less variation required only 100 models per condition, whereas up to 1000 were necessary for single crystal materials.

The high variability of the single crystal output originates from the large anisotropy of the elastic constants: c_{11}^{E}/c_{33}^{E} (~160%). The polycrystalline ceramic exhibits lower anisotropy (~104%), due to the statistical distribution of grain polarizations that remains after poling, averaging the tetragonal unit cell compliances. This suggests an advantage of using poled ceramic data, as it incorporates properties that are physically averaged as a function of microstructure.

With decreasing mesh size (m), the predicted elastic constants converge for the two electrical boundary conditions (Fig. 2).

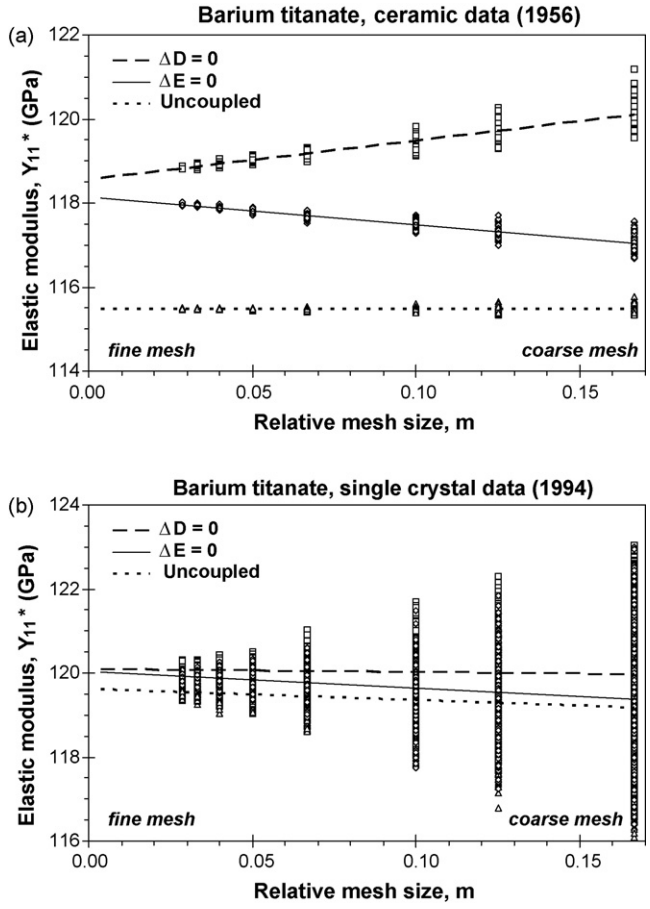

Fig. 2. Unpoled elastic modulus Y_{11}^{*} (GPa) for $BaTiO_3$ as a function of relative mesh size m, predicted by FE models with constant polarization or constant field constraints, or by an uncoupled model. Data points represent individual model outputs, with a linear regression applied to extrapolate to an infinitely fine mesh size ($m = 0$), to extract the modulus. The material data entered into the models are from (a) poled ceramic[14] or (b) single crystal barium titanate.[13]

The difference between constant field ($\Delta E = 0$), constant polarization ($\Delta D = 0$) and uncoupled results is more pronounced for the polycrystalline material. This can be attributed to the larger piezoelectric e_{33} and e_{31} constants, causing poor approximation of the unpoled state with coarsely modelled microstructures.

From the linear regression of the model data sets, the elastic constants at $m = 0$ (an infinitely fine microstructure) was extrapolated. This value was taken as the effective unpoled elastic constant. For example, from Fig. 2a the coupled model outputs converge at $m = 0$ to predict $Y_{11}^{*} \approx 118$ GPa.

Table 2 shows the elastic modulus for unpoled barium titanate, Y_{11}^{*} (GPa), as predicted by coupled and uncoupled FE modelling and the RoM average (Eq. (1)). The table shows the model predictions based on the input data for both single crystal and polycrystalline materials. An experimentally measured value was taken from the literature ($Y_{11}^{0} = 128$ GPa)[6] and the relative difference (%) between experimental and predicted results shown in parenthesis to aid comparison.

Good agreement between the uncoupled models and the RoM average for the ceramic materials provides initial confidence in these results. The RoM average becomes less reliable with single

Table 2
Elastic modulus for unpoled barium titanate, Y^*_{11}(GPa), as predicted by coupled and uncoupled FE modelling and a simple rule of mixtures average

Material input		
Ceramic 1956		
Coupled Y^*_{11}	118	(8%)
Uncoupled Y^*_{11}	115	(10%)
RoM average Y^*_{11}	115	(10%)
Ceramic 1999		
Coupled Y^*_{11}	117	(9%)
Uncoupled Y^*_{11}	114	(11%)
RoM average Y^*_{11}	114	(11%)
Monocrystal 1958		
Coupled Y^*_{11}	108	(16%)
Uncoupled Y^*_{11}	107	(16%)
RoM average Y^*_{11}	94	(27%)
Monocrystal 1994		
Coupled Y^*_{11}	120	(6%)
Uncoupled Y^*_{11}	120	(6%)
RoM average Y^*_{11}	108	(16%)

Percentage indicates difference from the experimentally measured value of $Y^0_{11} = 128$ GPa.[6]

crystal data, due to the large elastic anisotropies. The coupled models predict an unpoled stiffness in the range 108–120 GPa, which is typically 10% lower than the 128 GPa measured. However, in other experimental work a lower modulus of 107 GPa has been reported.[16] The largest error of 16% occurred when using the 1958 single crystal data,[11] which other authors have suggested as being inaccurate.[13]

Table 3 shows Poisson's ratio for unpoled barium titanate, ν^*_{12}, as predicted by coupled and uncoupled FE modelling and a RoM average. An experimentally measured value ($\nu^*_{12} = 0.35$)[6] was used to calculate the relative difference (%) between experimental and predicted results. The principle observation is that the coupled model prediction for Poisson's ratio is 3–17% different to the measured value, which is comparable to experimental variation in the measurement of ν^0_{12}. As previously stated, since the unpoled material is isotropic only the Young's modulus (Y^0_{11}) and Poisson's ratio (ν^0_{12}) is necessary to characterise the elastic properties.

Table 3
Poisson's ratio for unpoled barium titanate, ν^*_{12}, as predicted by coupled and uncoupled FE modelling and a simple rule of mixtures average

Material input		
Ceramic 1956		
Coupled ν^*_{12}	0.31	(11%)
Uncoupled ν^*_{12}	0.32	(9%)
RoM average ν^*_{12}	0.31	(11%)
Ceramic 1999		
Coupled ν^*_{12}	0.30	(14%)
Uncoupled ν^*_{12}	0.30	(14%)
RoM average ν^*_{12}	0.30	(14%)
Monocrystal 1958		
Coupled ν^*_{12}	0.41	(17%)
Uncoupled ν^*_{12}	0.41	(17%)
RoM average ν^*_{12}	0.31	(11%)
Monocrystal 1994		
Coupled ν^*_{12}	0.36	(3%)
Uncoupled ν^*_{12}	0.36	(3%)
RoM average ν^*_{12}	0.26	(26%)

Percentage indicates difference from the experimentally measured value of $\nu^*_{12} = 0.35$.[6]

4. Conclusion

The modelling technique developed in this work has demonstrated that unpoled elastic properties for barium titanate can be predicted using widely available poled piezoceramic data, with good agreement (∼10%) to the sparse experimental measurements. This efficient modelling approach enables large three-dimensional microstructures to be generated, which avoids inaccuracies of planar models and enables grains to be assigned various properties and aspect ratios for the study of textured microstructures, porosity effects and domain engineered materials.

The prediction of unpoled elastic constants by this technique is advantageous for commercial PZT based materials due to the lack of single crystal data. Knowledge of these material properties will assist the optimisation and design of novel piezoelectric devices with complex electrode geometries. Future work will compare model outputs with experimental data for PZT based compositions.

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