Stochastic optimization of electromechanical coupling in ferroelectric materials

K. P. Jayachandran, J. M. Guedes, H.C. Rodrigues

IDMEC-IST, Department of Mechanical Engineering, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal, jaya@dem.ist.utl.pt, jmguedes@ist.utl.pt, hcr@ist.utl.pt

1. Abstract
Polycrystalline ferroelectrics differ significantly from single crystals because of the presence of variously oriented grains or crystallites. The orientation of ferroelectric crystals plays a critical role in the anisotropy of their piezoelectric properties. The set of combination of variables, known as solution space, which dictates the orientation distribution of grains is unlimited. Thus a stochastic optimization combined with homogenization is employed for the identification of the optimal granular configuration of the ferroelectric ceramic microstructure with optimum electromechanical coupling suitable for applications such as transducers and actuators. The effective macroscopic electromechanical coupling \( k \) are calculated at every iteration using the mathematical homogenization method. The configuration of crystallites at each step is chosen by the optimization algorithm. The single crystal ferroelectrics are also investigated in an effort to compare the performance characteristics with that of polycrystals. A configuration constraining the orientation distribution of the \( c \)-axis (polar axis) of the crystallites is identified. This grain configuration would optimize the figures of merit such as \( d_h \) and \( k_h \) of the ferroelectric material.

2. Keywords: Stochastic Optimization, Homogenization, Ferroelectrics, Piezoelectricity, Coupled phenomena

3. Introduction
Ferroelectrics (FEs) have applications ranging from hydrophones to actuators and from ultrasonic generators to energy-harvesting devices due to its piezoelectricity (or electric-field-induced strain) [1-3]. The piezoelectric coupling coefficients which quantify the efficiency of a piezoelectric material in converting the electrical energy to the mechanical is ubiquitous figures of merit in such applications [1, 4]. Ferroelectrics in the polycrystalline form have an edge over the single crystals in engineering owing to the ease in manufacturing and the compositional modifications the former admits [5]. Many ferroelectric materials such as BaTiO\(_3\) exhibit an enhanced polarization if oriented away from the axis of their spontaneous polarization [3, 6, 7]. Noncollinear polarization rotation has been proposed as the possible origin of high piezoelectric response in FE single crystals [3, 7]. Furthermore, phenomenological thermodynamic theory addressing the piezoelectric anisotropy relates it to the flattening of the free energy function in certain nonpolar directions [5, 8].

As-grown polycrystalline FE is an aggregate of single crystalline grains with randomly oriented (spontaneous) polarizations [9]. The spatial configuration of crystallographic grains and their orientation distribution (texture) impact the piezoelectricity exhibited by conventional as well as new generation FEs [2]. The randomness in polarization-vector orientation renders the resultant piezoelectricity of the material to be marginal or zero. Attributing the resultant polarization is zero for as-grown polycrystal, an overall piezoelectricity can be enabled by the application of an external electric field, called poling field, though all the grains can never align perfectly [9].

The aggregate texture of an unpoled (as grown) polycrystal would have a uniform random distribution [10]. With the strength of the poling field increases, the nature of the grain orientation distribution becomes Gaussian (normal) [11]. Nevertheless, the spatial and orientational randomness of grains can be judiciously employed in the design of FE polycrystals (ceramics) with tailor-made configurations. Recently it is shown that overall piezoelectricity would be enhanced by the introduction of either [110]- or [111]-oriented grains into a random BaTiO\(_3\) polycrystal [12]. The piezoelectric coefficient \( d_{33} \) scales up until a certain grain size and further decrease from this point would decrease the \( d_{33} \) in these experiments. Though the ceramics possess randomly oriented grains, fine domains must be introduced to achieve this narrow window of high piezoelectric activity. Despite intense research in ferroelectrics, the solution of an optimal grain configuration of the polycrystalline FE is hardly resolved. This is mainly due to the vast number of possible configurations available at hand albeit the FE ceramics are easy to manufacture. This paper is concerned with optimally designing the performance characteristics of the piezoelectric component in a hydroacoustic application such as a hydrophone. We would identify an optimum configuration of grains in the microstructure of a polycrystalline FE material with an enhanced electromechanical coupling from both a textured ceramic and a single crystal.
To arrive at an optimum texture of the ferroelectric polycrystal at which the material exhibits maximum piezoelectric performance as a hydrostatic transducer material, a global optimization method has to be employed [13]. Stochastic optimization techniques like simulated annealing (SA) are quite suitable in this respect as the objective function is not sensitive to the starting point of the iterative process. Besides being insensitive to the starting point, SA can search a large solution space and they can escape local optimum points thanks to the freedom for occasional uphill moves. Kirkpatrick et al. [14] first proposed simulated annealing as a powerful stochastic optimization technique. The complex structure of configuration space is treated analogous to the state of material controllable by an adjustable parameter, the temperature, in simulated annealing. In other words, annealing is a strategy by which an optimum state can be approached by controlling the temperature. Annealing involves heating the material matrix to high temperature and then let it be cooled slowly so that at each step a near thermal equilibrium is achieved and finally render the material to a stable minimum energy crystalline (ordered) state. The idea to explore analogy of the annealing used in solid state physics with the optimization problems gives rise to simulated annealing technique. A control parameter similar to the temperature in physical annealing is introduced in optimization which will dictate the number of states to be accessed in going through the successive steps of the optimization algorithm before being settled in the minimum energy state (the optimum configuration).

4. Model setup
As remarked above, the crystallographic grains (crystallites) in an as-grown polycrystal are randomly oriented and require three angles to describe its orientation with reference to a fixed Cartesian coordinate system. Euler angles ($\varphi$, $\theta$, $\psi$) can completely specify the orientation of the crystallographic coordinate system embedded in crystallites and thereby the orientation of crystallites [15].

4.1. Design variables
The aggregate texture for polycrystalline ferroelectrics follows a Gaussian distribution the probability distribution function (pdf) is defined as,

$$f(\alpha \mid \mu, \sigma) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{(\alpha - \mu)^2}{2\sigma^2}\right)$$

with the direction of the electric field as the origin. Here $\mu$ and $\sigma$ are the parameters of the distribution viz., the mean and the standard deviation respectively. $\alpha$ stands for the Euler angle ($\varphi$, $\theta$, $\psi$). In a 3D case as in the present work, parameters $\mu$ and $\sigma$ perform the role of the control parameters which will decide the scatter of the orientations (Euler angles) and hence be critical to the piezoelectric response of the polycrystalline ferroelectric material. Hence $\mu$ and $\sigma$ are the design variables of the optimization problem. Thus we are aiming to find an optimum set of these parameters from a solution space controlled by the laws of coordinate transformations from a crystallographic coordinate system embedded in the grains to a local coordinate system which coincides with the global frame of reference. Also, the solution space is bounded by distribution parameters $\mu$ and $\sigma$ ranging from those of uniform (in the case of random polycrystal) to those of Gaussian distribution (in the case of poled polycrystal). A fairly uniform kind of distribution can be achieved by putting standard deviation ($\sigma$) equals 5 and for a poled ceramic ferroelectric the $\sigma$ is set near zero.

4.2. Objective function
The composite piezoelectric materials found useful application in transducers for hydroacoustic applications [16, 17]. There are several requirements for the piezoelectric used in these transducers. A major requirement for a sensitive transducer is that the piezoelectric material used in the composite must efficiently convert between electrical and mechanical energy. Effective piezoelectric constants and hydrostatic figures of merit such as the hydrostatic charge response $d_h$, and hydrostatic coupling constant $k_h$ manifest the piezoelectric sensitivity in hydroacoustic applications among other parameters [17, 18]. In single crystalline materials like BaTiO$_3$, the piezoelectric strain shows a maximum when they are poled along a nonpolar axis [3, 6]. However, our objective is to search possible ways of enhancing the piezoelectricity in ceramic ferroelectric materials making it suitable for hydroacoustic applications. Given the difficulties in synthesizing good quality single crystals of fairly large size for integration and also the non-reliability of reproduction, polycrystals are often preferred to single crystals in device applications. In polycrystalline piezoelectric materials, the state of strain is inhomogeneous. Understanding the local and global ferroelectric response of these topologically complex materials by combining mathematical modeling and simulation could help effectively engineer material configurations and judicious selection of materials. The grain distribution parameters chosen by the simulated annealing (SA) algorithm will prompt a normal random generator thereby create a set of Euler angles ($\varphi$, $\theta$, $\psi$). These Euler angles will dictate the coordinate transformation in the electromechanical property tensors appearing in the homogenization equations.
4.3. Homogenization of piezoelectric material
We have used mathematical homogenization method for the evaluation of the equilibrium, effective (macroscopic) piezoelectric and mechanical properties of a polycrystalline ferroelectric material possessing the lowest crystallographic symmetry. Further, the numerical solution of the coupled piezoelectric problems is sought using the finite element method (FEM) to eventually compute the homogenized coefficients. The mathematical theory of the homogenization method accommodates the interaction of different phases in characterizing both the macro- and the micromechanical behaviors [19]. In homogenization theory it is usually assumed that the material is locally formed by the spatial repetition of very small microstructures, when compared with the overall macroscopic dimensions. Further, it is assumed that the material properties are periodic functions of the microscopic variable, where the period is very small compared with the macroscopic variable. This assumption enables the computation of equivalent material properties by a limiting process wherein the microscopic cell size is approaching zero [20]. The finite element method used for this study correlates each randomly oriented grain in a polycrystalline material with each element of the finite element mesh. Each grain in a polycrystalline material is assumed to be made of a single, pinned, chemically homogeneous ferroelectric domain.

The asymptotic analysis and homogenization of the piezoelectric medium [21, 22] has resulted in the macroscopic piezoelectric coefficients

\[
e^H_{prs}(x) = \frac{1}{y} \left\{ \int \left[ e_{ijkl}^0(x, y) \left( \delta_{kp}^0 + \frac{\partial R(p)}{\partial y_k} \right) \delta_{jq}^0 \frac{\partial \chi_{ij}}{\partial y_j} + \frac{\partial \psi_{ij}}{\partial y_j} \right] - e_{ijkl}(x, y) \frac{\partial \Phi_{ij}(p)}{\partial y_j} \right\} dY \right\}
\]

in index notation. Here \( e_{ijkl}^0 \) are the piezoelectric stress coefficients of the single grain and a number of such distinct grains constitute the unit-cell. \( \chi_{ij}^{(rs)} \) is a characteristic displacement, \( R(p) \) is a characteristic electric potential, \( \Phi_{ij}^{(p)} \) and \( \psi_{ij}^{(rs)} \) are characteristic coupled functions and \( Y \) is the size of the unit-cell. \( \delta \) is the Kronecker delta symbol. Symmetry requires that \( e_{ijkl}^H = e_{ijlk}^H \). Also in contracted notation \( e_{ij}^H \) can be written as \( e_{i\mu}^H \) where \( i,j,k = 1,2,3 \) and \( \mu = 1,2,..6 \) in the general three-dimensional case. The functions \( e_{ij}^H \) in Eq. (2) can be described in microscopic coordinate system \( y_i \) using the components of Euler transform tensors from crystallographic coordinates. The homogenized electromechanical properties which are the objectives of this study are the following:

The piezoelectric strain coefficients,

\[
d_{H} = \sum_{\mu=1}^{6} e_{i\mu}^H s_{i\mu}^H
\]

where \( s_{i\mu}^H \) are the homogenized elastic compliance tensor. The hydrostatic charge response,

\[
a_{H} = d_{H} + 2e_{H}^{31}
\]

and the hydrostatic coupling coefficient,

\[
k_{H} = d_{H} \sqrt{T H E H E H s_{h}}^{33}
\]

where \( e_{33}^T \) is the unclamped (zero stress) dielectric permittivity and \( s_{h}^{E} \) is the hydrostatic compliance defined by,

\[
s_{h}^{E} = 2(s_{11}^{E} + s_{12}^{E} + s_{13}^{E} + s_{23}^{E} + s_{33}^{E}) + s_{33}^{E}
\]

The piezoelectric response is determined along an arbitrary crystallographic direction determined by the Euler angles with respect to the reference frame of the unit-cell. The superscript \( H \) would be dropped henceforth from the homogenized coefficients for brevity.

The numerical model for this work is developed in 3D incorporating the anisotropy of the polycrystalline ferroelectric at the grain level. The microscopic system of equations is computationally solved using the FEM. Since our model is able to predict the macroscopic electromechanical coefficients of all piezoelectric crystal classes, application of the same to ferroelectric BaTiO3 requires the knowledge of point group symmetry which is tetragonal \( 4mm \). The unit-cell is discretized using a mesh of \( 14 \times 14 \times 14 \) finite elements and each node of the trilinear solid element is allowed four degrees of freedom (one electric potential and three displacements). Full integration (2-point Gaussian integration rule in each direction) is used for the evaluation of the stiffness, piezoelectric and dielectric matrices and for the homogenization. As the representative unit-cell is expected to
capture the response of the entire piezoelectric system, particular care is taken to ensure that the deformation across the boundaries of the cell is compatible with the deformation of adjacent cells. Hence all the load cases are solved by enforcing periodic boundary conditions in the unit-cell for the displacements and electrical potentials. The numerical simulation of ceramic BaTiO$_3$ are done using the parameters of single crystal data from Ref. [23] using the present homogenization model computationally implemented in Fortran.

5. Simulated Annealing

The basic concept of SA is based on the Metropolis algorithm (Metropolis et al. [24]) for simulating the behavior of an ensemble of atoms that are cooled slowly from their melted state to the minimum energy ground state. The ground state or minimum energy state corresponds to the global optimum we are seeking in material optimization. In order to apply SA to a piezoelectric material, we must first introduce the notion of ‘system energy.’ In order to be consistent with our definition of design variables, let

$$E(R) = \gamma(\alpha) = \gamma(\sigma, \mu)$$  \hspace{1cm} (7)

be the surrogate for energy of a particular configuration $R$. Here $\sigma \in [0, 5]$ and $\mu \in [0, \pi/2]$. The distribution parameters are selected from a random set. $\gamma$ is the objective function in our optimization problem.

The ultimate goal of SA is to find the ground state(s), i.e., the minimum energy configuration(s), with a relatively small amount of computation. Minimum energy states are those that have a high likelihood of existence at low temperature. The likelihood that a configuration, $R$, is allowed to exist is equal to the Boltzmann probability factor,

$$P(R) = \exp \left[ -\frac{E(R)}{k_B T} \right]$$  \hspace{1cm} (8)

where $k_B$ is the Boltzmann constant and $T$ is the temperature. For computational convenience $k_B$ is often treated as unity. It is obvious from the above relation that as the temperature decreases, the Boltzmann distribution concentrate on the states with lowest energy and finally, when the temperature approaches zero, only the minimum energy states have the non-zero probability of occurrence. However, it is well-known (Kirkpatrick et al. [14]) that if the cooling is too rapid, i.e., if the solid is not allowed to reach thermal equilibrium for each temperature value, defects can be 'frozen' into the solid and metastable amorphous states can be reached rather than the low energy crystalline lattice structure.

To simulate the evolution of thermal equilibrium of a solid for a fixed $T$, Metropolis et al. [24] proposed a Monte Carlo method, which generates a sequence of states of the solid. Given the current state of energy $E_1$, another set of design variables are randomly generated which will eventually calculates the another energy $E_2$. If the difference in energy $\Delta E$, between the current state and the new state ($E_2 - E_1$) is positive (negative in the case of minimization) then the process is continued with the new state. If $\Delta E \leq 0$ then the probability of acceptance of the new state is given by $\exp(\Delta E / k_B T)$ for maximization problems as in the present work. Following this criterion the system eventually evolves into thermal equilibrium. Once thermodynamic balance is reached at a given temperature the temperature is lowered slightly and new chain of iterations will be executed before the system finally ends up in equilibrium.

6. Results and discussion

Simulated annealing (SA) algorithm requires homogenized coefficients at each iteration step. It is implemented in Matlab. We have created an interface to call Fortran from Matlab for the purpose of calling homogenization algorithm into SA. As stated above we have six design variables, viz. $\sigma, \phi, \mu, \sigma, \phi, \mu$ and $\mu$ that corresponds the standard deviations and means of the Euler angles $(\phi, \theta, \psi)$ expressed in radians. The temperature $T$ is set to fall by 20% from each of the previous step, i.e., $T_{k+1} = 0.8T_k$. Ideally we must start the iteration with an initial guess of the design variables randomly picked up from $\sigma \in [0, 5]$ and $\mu \in [0, \pi/2]$.

First we have applied this optimization procedure to the case of single crystal BaTiO$_3$. Thus we started with Euler angles $(\phi, \theta, \psi)$ alone without going to the assumption of distribution of grain orientations since a single crystal has no grain structure. All the three angles are allowed values between limits $-\pi \leq (\phi, \theta, \psi) \leq +\pi$. Here the optimization problem can be summarized as to find the value of $\lambda$ which maximizes
\[ f(\lambda) = E \]

subject to

\[ -\pi \leq \lambda = (\phi, \theta, \psi) \leq \pi \]

Here \( E \) is any of the objective function we mentioned in this text. First we study the piezoelectricity BaTiO\(_3\) single crystal. The evolution of the objective function \( d_{33} \) with the temperature is shown in Fig.1. The piezoelectric coefficient \( d_{33} \) obtained after optimization is 223.7 pC/N which compares exactly with our homogenization results reported recently [25]. The solution \((\phi, \theta, \psi)\) is \((-2.182, 0.873, -0.175)\). This corresponds to \((\phi = -125^\circ, \theta = 50^\circ, \psi = -10^\circ)\). This is one of the parallel \langle 111 \rangle\) directions of the BaTiO\(_3\) single crystal along which the maximum piezoelectric coefficient of \( d_{33} = 203\) pC/N is measured by Wada et al. [26].

Figure 1: “Energy” (piezoelectric coefficient \( d_{33} \)) as a function of temperature in ferroelectric single crystal BaTiO\(_3\). The diamond indicates the experimental value obtained in Ref. [26] for [111] oriented single crystals.

Figure 2: “Energy” (hydrostatic charge response \( d_h \)) as a function of temperature and number of iterations in ferroelectric single crystal BaTiO\(_3\).

Fig. 2 illustrates the results of optimization corresponding to the hydrostatic charge response \( d_h \) in BaTiO\(_3\) single
crystal. As shown in Eq. 4, this property depends on the transverse piezoelectric coefficient (which in general is negative) $d_{31}$. Hence it would be certainly less than the maximum $d_{33}$ one can get from the system. Here it attains a maximum of $d_h = 181.8$ pC/N at the optimal solution of $(\phi = 110^\circ, \theta = 55^\circ, \psi = 0^\circ)$. This direction will also coincide with one of the <111> orientations of the BaTiO$_3$ single crystal. Next we study the optimization of electromechanical coupling $k_h$ in single crystal BaTiO$_3$. Fig. 3 shows the convergence of the coupling coefficient $k_h$ of single crystal BaTiO$_3$ with the number of iterations and decreasing temperature. The optimum value is $k_h = 0.55$ at $(\phi = 75^\circ, \theta = 40^\circ, \psi = 5^\circ)$.

![Figure 3: “Energy” (hydrostatic coupling coefficient $k_h$) as a function of temperature and number of iterations in ferroelectric single crystal BaTiO$_3$](image1)

![Figure 4: “Energy” (Piezoelectric coefficient $d_{33}$) as a function of temperature in ferroelectric polycrystal BaTiO$_3$. The horizontal line gives the experimental value for [111] oriented single crystal from Ref. [26].](image2)

Next, we apply this optimization procedure to the ferroelectric polycrystals. The optimization problem in polycrystal ferroelectrics can be summarized as to find the value of $\lambda$ which maximizes
\[
\begin{align*}
\text{subject to} \\
0 &\leq \lambda = (\mu_\phi, \mu_\theta, \mu_\psi) \leq \pi/2 \\
0 &\leq \lambda = (\sigma_\phi, \sigma_\theta, \sigma_\psi) \leq 5 
\end{align*}
\] (10)

where \( E \) is the objective function. First we start the optimization keeping the angles \( \phi \) and \( \psi \) at zero by keeping \( \sigma_\phi, \mu_\phi, \sigma_\psi \) and \( \mu_\psi \) at zero. The piezoelectric coefficient obtained after the optimization is \( d_{33} = 236.4 \) pC/N after 140 iterations. The solution \((\sigma_\phi, \mu_\phi, \sigma_\theta, \mu_\theta, \sigma_\psi, \mu_\psi) = (0, 0, 0.5, 0, 0, 0)\). It must be noted that here we already set the angles \( \phi \) and \( \psi \) at zero so that \((\sigma_\phi, \mu_\phi, \sigma_\psi, \mu_\psi) = (0, 0, 0, 0)\). The quality of the results was verified against different initial configurations. This result is significant in itself that the value of \( d_{33} = 236.4 \) pC/N is for polycrystalline \( \text{BaTiO}_3 \). The maximum value of the piezoelectric strain obtained experimentally for single crystals oriented along [111] direction is \( d_{33} = 203 \) pC/N [26]. The solution implies that a FE ceramic having its crystallites all aligned with respect to the vertical axis but with a standard deviation of 0.5 from it can be a better piezoelectric than oriented single crystals.

Next, we analyze the case with \((\sigma_\phi, \mu_\phi, \sigma_\theta, \mu_\theta, \sigma_\psi, \mu_\psi) \in [0, 5] \) and \((\mu_\phi, \mu_\theta, \mu_\psi) \in [0, \pi/2]\). The results are shown in Fig.4. The solution \((\sigma_\phi, \mu_\phi, \sigma_\theta, \mu_\theta, \sigma_\psi, \mu_\psi) \) obtained is \((4.7, 0.873, 0, 0.698, 1.8, 1.223)\). The objective function converges with a value \( d_{33} = 273.7 \) pC/N which is very much higher than both [001] poled and [111] poled single crystals. This supplements the notion that randomness in the orientation of grains, if utilized judiciously, might be useful for manufacturing ceramics with better piezoelectric performance than single crystals. The solution suggests to keep the Euler angle related to the orientation of \( ab \)-plane of the crystallites (\( \phi \) and \( \psi \)) to be kept in random rather than keeping their value at zero while the orientation \( \theta \), of \( c \)-axes is kept at 0.698 radians (= 40°). Such a configuration of the crystallites in a ceramic FE would result in a better piezoelectric than an oriented single crystal. Fig. 5 depicts the optimization results of hydrostatic charge response \( d_h \) of the polycrystal ferroelectric \( \text{BaTiO}_3 \). Here the optimum value obtained is \( d_h = 189.20 \) pC/N with a solution \((\sigma_\phi, \mu_\phi, \sigma_\theta, \mu_\theta, \sigma_\psi, \mu_\psi) \) equal to \((0, 0, 0.6, 0.087, 0)\). This value of \( d_h \) is higher than the single crystal maximum charge response of \( d_h = 181.8 \) pC/N. In summary, tailoring the microstructure by tuning the texture of the ferroelectrics would result in materials possessing piezoelectric properties better than single crystals. In view of the difficulties associated with the manufacture of the single crystals, the present result would bear importance in applications involving piezoelectricity.
Acknowledgements
KPJ acknowledges the award of Ciência 2007 by FCT, Portugal.

References