Optimal configuration of microstructure in ferroelectric materials by stochastic optimization

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An optimization procedure determining the ideal configuration at the microstructural level of ferroelectric (FE) materials is applied to maximize piezoelectricity. Piezoelectricity in ceramic FEs differ significantly from that of single crystals because of the presence of crystallites (grains) possessing crystallographic axes aligned imperfectly. The piezoelectric properties of a polycrystalline (ceramic) FE is inextricably related to the grain orientation distribution (texture). The set of combination of variables, known as solution space, which dictates the texture of a ceramic is unlimited and hence the choice of the optimal solution which maximizes the piezoelectricity is complicated. Thus a stochastic global optimization combined with homogenization is employed for the identification of the optimal granular configuration of the FE ceramic microstructure with optimum piezoelectric properties. The macroscopic equilibrium piezoelectric properties of polycrystalline FE is calculated using mathematical homogenization at each iteration step. The configuration of grains characterised by its orientations at each iteration is generated using a randomly selected set of orientation distribution parameters. The optimization procedure applied to the single crystalline phase compares well with the experimental data. Apparent enhancement of piezoelectric coefficient $d_{33}$ is observed in an optimally oriented BaTiO$_3$ single crystal. Based on the good agreement of results with the published data in single crystals, we proceed to apply the methodology in polycrystals. A configuration of crystallites, simultaneously constraining the orientation distribution of the c-axis (polar axis) while incorporating ab-plane randomness, which would multiply the overall piezoelectricity in ceramic BaTiO$_3$ is also identified. The orientation distribution of the c-axes is found to be a narrow Gaussian distribution centred around 45°. The piezoelectric coefficient in such a ceramic is found to be nearly three times as that of the single crystal. Our optimization model provide designs for materials with enhanced piezoelectric performance, which would stimulate further studies involving materials possessing higher spontaneous polarization.

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I. INTRODUCTION

Ferroelectrics (FEs) have plethora of applications from actuators to sensors and from ultrasonic generators to energy-harvesting devices due to its piezoelectricity (or electric-field-induced strain)\textsuperscript{1,2}. The piezoelectric coefficients $d$, which quantify the piezoelectric strain of an applied electric field, are the ubiquitous figures of merit in such applications\textsuperscript{3,4,5}. Optimization of these parameters in single crystals and nanoparticles compounds with the existing deleterious effects such as twinning and depoling though many of them exhibit enhancement of piezoelectricity in certain nonpolar directions\textsuperscript{6,7}. (Here nonpolar in the sense that a direction other than the spontaneous polarization direction of the crystal). Nonetheless, FEs in the polycrystalline form are preferred over the single crystals in engineering owing to the ease in manufacturing and the compositional modifications of polycrystals\textsuperscript{8}. Noncollinear polarization rotation has been proposed as the possible origin of high piezoelectric response in FE single crystals\textsuperscript{9,10}. Furthermore, phenomenological thermodynamic theory addressing the piezoelectric anisotropy relates it to the flattening of the free energy function in certain nonpolar directions\textsuperscript{11,12,13}.

As-grown polycrystalline FE is an aggregate of single crystalline grains with randomly oriented (spontaneous) polarizations\textsuperscript{14}. The spatial configuration of crystallographic grains and their orientation distribution (texture) impact the piezoelectricity exhibited by conventional as well as new generation FEs\textsuperscript{15}. The randomness in polarization-vector orientation renders the resultant piezoelectricity of the material to be marginal or zero. Although 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\textsuperscript{14,15}.

The aggregate texture of an unpoled polycrystal would have a uniform random distribution of orientation\textsuperscript{14,15}. With the strength of the poling field increases, we assume the nature of the grain orientation distribution to become Gaussian (normal)\textsuperscript{16,17}. Piezoforce microscopic image studies of Pb(Zr,Ti)O$_3$ (or PZT) films lead also to a quantitatively similar kind of distribution of domains\textsuperscript{18}. Spherical harmonics based orientation distribution function (ODF) is also used to model the texture of polycrystalline ferroelectrics\textsuperscript{19,20}. The texture analysis of PZT by synchrotron X-ray diffraction reveals that the diffraction peak intensity ratio $R(200)$ shows a strong dependence on $\sin^2 \theta$, where $\theta$ represents the orientation angle between the plane normal and the polar axis of the material\textsuperscript{21}. Moreover, the domain distribution has been treated statistically to be in an orientation distribution characterised with March-Dollase function in X-ray and neutron diffraction studies of piezoelectric materials\textsuperscript{22}. In this work, Rogan et al.\textsuperscript{23} has done in situ neutron
The crystal orientation and thus the piezoelectric properties would therefore inextricably depend on three Euler angles. Even in the case of single crystals it would be tedious to survey all the crystallographic orientations and resolved although much research activity is underway in ferroelectrics. This is mainly due to the vast number of possible configurations available at hand albeit the FE ceramics are easy to manufacture. In this work we would identify an optimum configuration of grains in the microstructure of a polycrystalline FE material with an enhanced piezoelectricity from both a textured ceramic and a single crystal. Moreover, we would discuss on the mechanism of polarization rotation in FEs in view of their piezoelectric response in the context of the optimization results.

For many FE single crystals, the polarization \( \mathbf{P} \) rotates with an electric field applied along a nonpolar direction and the polarization rotation in such cases does not necessarily evolve through a monoclinic phase. The polarization \( P_i = d_{ij}T_{ij} \), where \( T \) is the stress and \( d \) piezoelectric strain coefficient. Here the Latin indices range from 1 to 3 and Greek indices from 1 to 6, owing to the Voigt contraction of tensorial indices. The typical value of the piezoelectric coefficient \( d_{33} \) measured for tetragonal (T) BaTiO\(_3\) is \( \approx 90 \) pC/N when [001]-poled while \( d_{33} \approx 203 \) pC/N for [111]-poled engineered-domain single crystal. The piezoelectric coefficient \( d_{31} \) typically falls between -33.4 and -62.0 pC/N for [001]- and [111]-poled single domain BaTiO\(_3\) crystals. Since templated grain growth enables the fabrication of textured ceramics with a fraction of oriented material, it is important to find out the degree of orientation as well as the fraction of aligned grains in a matrix of random polycrystalline FE. Pb-free \((K_{0.3}Na_{0.5})(Nb_{0.9}Sb_{0.03})O_{3}\) polycrystal grown using this method is recently shown to possess excellent electromechanical properties if it is (001)-oriented with a narrow orientation distribution. Such a possibility to fabricate useful polycrystals is one of the motivations to a continuum model study, as is shown in this paper.

The orientation of a piezoelectric crystal is modeled by a set of Euler angles \((\phi, \theta, \psi)\). Euler angles are defined in the following ways: first, the crystal is rotated by angle \( \phi \) around the z-axis, then rotate an angle \( \theta \) around the new x-axis, and finally by an angle \( \psi \) around the new z-axis. All the rotations are in the counterclockwise direction. The matrix of transformation from the crystallographic coordinate system to a local coordinate system \( \mathbf{y} \) is given by:

\[
a_{ij} = \begin{pmatrix}
cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi & \cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi & sin \phi \sin \theta \\
-\sin \psi \cos \phi - \cos \theta \sin \phi \cos \psi & -\sin \psi \sin \phi + \cos \theta \cos \phi \cos \psi & cos \phi \sin \theta \\
\sin \theta \sin \phi & -\sin \theta \cos \phi & \cos \theta 
\end{pmatrix}
\] (1)
map the corresponding piezoelectric properties. This situation demands an optimization procedure to realize a particular objective function in a piezoelectric material. [There would be $73^3 = 389,017$ different combinations of $(\phi, \theta, \psi)$ if one chose angles at an interval of $5^\circ$ between $\pm \pi$ in FE single crystals alone]. Nonetheless, the case of polycrystals is too complicated as it is constituted ideally by thousands of single crystalline grains. To arrive at an optimum texture of the ferroelectric polycrystal at which the material exhibits maximum piezoelectric performance, a global optimization method has to be employed here as well. This is because the piezoelectricity depends on the parameters which controls the orientation distribution of the grains. Nevertheless, the choice of the optimal set of parameters is complicated and it is impossible to analyze all possible combinations of the distribution parameters or the angles themselves. We chose a modified stochastic global optimization technique incorporating a generalised Monte Carlo scheme for this purpose. A modified simulated annealing (SA) is quite suitable in this respect as the objective function is not sensitive to the starting point of the iterative process (the so called connectivity, where any state of the system can be reached starting from any other state).

We propose a design strategy based on a continuum mechanics and modeling to attain electromechanic figures of merit in FEs combined with a modified simulated annealing for optimization, in this paper. The model is developed for crystals of all classes. In this paper, we apply this methodology to optimize the piezoelectricity in the classic perovskite, the tetragonal $P4mm \text{ BaTiO}_3$. The piezoelectric performance is quantified through the evaluation of the effective electromechanical properties of the FE single crystals and polycrystals. We have used the mathematical homogenization method which efficiently characterizes the equilibrium macroscopic electromechanical properties of a polycrystalline ferroelectric material.

II. MODEL

A. Homogenization of ferroelectrics

The electrical and elastic boundary conditions and the orientation of the polarization and permitivity axes of grains (in polycrystals) and crystals complicate the microscopic analysis of the FEs. Considering these, the mathematical modeling (if we describe the rapidly varying material properties with equally rapidly varying functions) and the numerical analysis of these materials will become difficult and sometimes even intractable. To put it simply, homogenization of partial differential equations (PDEs) has as its main purpose to approximate PDEs that have rapidly varying coefficients with equivalent homogenized PDEs that (for instance) more easily lend themselves to numerical treatment in a computer. The homogenization method accommodates the interaction of different phases in characterizing both the macro- and the micro-mechanical behaviors. (For instance, in a polycrystalline material the crystallite manifests as a phase in this sense). In homogenization theory the material is locally formed by the spatial repetition of very small microstructures (unit-cells), when compared with the overall macroscopic dimensions. Further, the material properties are periodic functions of the microscopic variable, where the period is very small compared with the macroscopic variable. This enables the computation of equivalent material properties by a limiting process wherein the microscopic cell size is approaching zero.

The key idea in micromechanical modeling is to relate the effective properties of a material to the properties of its constituent parts, which may be the phases of a composite or the grains of a polycrystal in ferroelectrics. A review on the various methods for obtaining effective properties of ferroelectrics is given in an earlier paper. The asymptotic analysis and homogenization of the piezoelectric medium has resulted in the equilibrium macroscopic piezoelectric properties in tensor notation as follows:

$$e_{pr,s}^H(x) = \frac{1}{|Y|} \int_Y \left[ e_{kij}(x, y) \left( \delta_{kp} + \frac{\partial R_p}{\partial y_k} \right) \delta_{ij} + \frac{\partial R_p}{\partial y_k} \right] dY$$

$$\kappa_{pq}^H(x) = \frac{1}{|Y|} \int_Y \left[ \kappa_{ij}(x, y) \left( \delta_{ip} + \frac{\partial R_p}{\partial y_i} \right) \delta_{jq} + \frac{\partial R_p}{\partial y_k} \right] dY$$

$$C_{rs}^{E_{pq}}(x) = \frac{1}{|Y|} \int_Y \left[ C_{ijkl}^{E_{pq}}(x, y) \left( \delta_{ipl} \delta_{jq} + \frac{\partial X_{pq}^i}{\partial y_j} \right) \right]$$

$$+ e_{kij}(x, y) \left( \delta_{ip} \delta_{jq} + \frac{\partial X_{pq}^i}{\partial y_j} \right) dY$$

Here the $e$, $\kappa$ and $C$ are the electromechanical coefficients, viz., piezoelectric, dielectric and elastic stiffness coefficients respectively. Also, $\chi_{rs}(x, y)$ is the characteristic displacement, $R(x, y)$ is the characteristic electric potential, $\Phi_{rs}(x, y)$ and $\psi_{rs}(x, y)$ are characteristic coupled functions of the FE unit-cell of size $Y$, satisfying a set of microscopic equations. $\delta$ is the Kronecker delta symbol. (We have assumed Einstein summation convention that repeated indices are implicitly summed over throughout this paper). Symmetry requires that $e_{kij} = e_{kji}$, $\kappa_{ij}^r = \kappa_{ji}^r$ and $C_{pq}^{E_{ij}} = C_{pq}^{E_{ji}}$. In the above Eqs. $[2]-[4]$ $e_{kij}(x, y)$, $\kappa_{ij}^r(x, y)$ and $C_{pq}^{E_{ij}}(x, y)$ are the electromechanical properties of the single crystallite whose collection constitutes the microscopic unit-cell and can be described in microscopic coordinates $y$ as
$$C_{ijkl}^E = a_{ip}a_{jq}a_{kr}a_{ls}C_{pqrs}^{E'}$$
$$\kappa_{ij} = a_{ip}a_{jq}\kappa_{ij}'$$
$$\varepsilon_{ijk} = a_{ip}a_{jq}a_{kr}\varepsilon_{pqrs}$$

(5)

where $a_{ij}$ are the Euler transformation tensors from crystallographic coordinate system to the local microscopic coordinates $y^m$. Here the primed moduli are the ones expressed in crystallographic coordinate system. Also the piezoelectric response is determined along an arbitrary crystallographic direction determined by the Euler angle $(\phi, \theta, \psi)$ with respect to the reference frame of the microstructure, i.e., $y$. [Here the microstructure refers to the representative volume element (RVE) of the ferroelectric polycrystal used for the homogenization]. The (resultant) polarizations of the crystallites in an as-grown polycrystal are randomly oriented in the lattice space and hence require three angles to describe its orientation with reference to a fixed coordinate system. Euler angles $\phi$, $\theta$ and $\psi$ can completely specify the orientation of the crystallographic coordinate system embedded in crystallites and thereby the orientation of relative to a fixed Cartesian coordinate system. (The superscript $H$ would be dropped from the homogenized piezoelectric properties given in Eqs. (2)-(4) for brevity from the rest of the discussion).

After asymptotic analysis a set of microscopic system of equations characterising $\chi^*_i$ ($x,y$), $R_i(x,y)$, $\Phi_i(x,y)$ and $\psi_{rs}(x,y)$ is obtained and is solved computationally. The three-dimensional (3D) numerical model developed is implemented in finite element method (FEM). The polycrystal sampling is performed using a unit-cell of $14 \times 14 \times 14$ mesh with 21,952 Gaussian integration points. The convergence of piezoelectric properties with unit-cell size allows us to determine the simulation-space-independent, macroscopic piezoelectric properties at various distribution of grains. Also the convergence studies are necessary as the orientations (Euler angles) of the crystallites are chosen randomly from a Gaussian distribution of angles. A normal random generator delivers different sets of numbers each time it is invoked and this will affect the consistency of the results. Nonetheless, at a $14^3$ mesh we found that the statistical fluctuations on $d_{ij\mu}$ are less than 4% (Ref. 20). After using the usual approximations of FEM, the set of linear equations for each load case is obtained where each global stiffness, piezoelectric and dielectric matrix is the assembly of each element's individual matrix, and the global force and charge vectors are the assembly of individual force vectors for all the elements.

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 microstructure (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. Thus all the load cases are solved by enforcing periodic boundary conditions in the unit-cell for the displacements and electrical potentials. Though the model is general and is designed to accommodate all crystalline symmetries, we apply it to the case of BaTiO$_3$. The numerical homogenization of ceramic BaTiO$_3$ is carried out using the single crystal data taken from Ref. [32] using the present homogenization model.

B. Optimization of piezoelectricity

The texture of a polycrystalline ceramic can be quantified through the distribution parameters corresponding to the angle of orientation in space. Euler angles $(\phi, \theta, \psi)$ can completely specify the orientation of the crystallographic coordinate system embedded in crystallites and thereby their orientations with respect to a local coordinate system $y_i$. Since the aggregate texture for polycrystalline FEs follows a Gaussian distribution, the probability distribution function (pdf) is defined by,

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

(6)

about the direction of the electric field. $\mu$ and $\sigma$ are the parameters of the distribution viz., the mean and the standard deviation respectively. $\alpha$ stands for the Euler angles $(\phi, \theta, \psi)$. Since $\mu$ and $\sigma$ decide the scatter of orientations (of the grains) and for that matter be critical to the piezoelectric response of an FE ceramic, they would assume the role of 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 ranging from those of uniform (in the case of random polycrystal) to those of normal distribution (in the case of poled polycrystal). A fairly uniform distribution can be achieved by putting standard deviation ($\sigma$) equals 5 and for a poled ceramic ferroelectric the $\sigma$ is set near zero.

Here the objective is to search possible ways of enhancing the piezoelectricity in FE polycrystals. When an electric field is applied in a piezoelectric crystal the shape of the crystal changes slightly. This is known as the converse piezoelectricity. There exists a linear relationship between the components of the electric field vector $E_i$ and the components of the strain tensor $\varepsilon_{ij}$ which describe the change in shape of the piezoelectric strain constant $d_{ij\mu}$, (which is written in tensor form as $\varepsilon_{ij} = d_{ij\mu} E_{\mu}$) thus quantifies the piezoelectricity of a FE material. In a ceramic FE each of the three Euler angles $\phi, \theta$ and $\psi$ if observed individually falls in respective normal distributions thanks to the misalignment of the crystallographic axes of the constituent grains. Hence
there would be six (3 pairs) parameters altogether viz., 
\((\mu_\phi, \sigma_\phi), (\mu_\theta, \sigma_\theta)\) and \((\mu_\psi, \sigma_\psi)\) quantifying the scatter of angles from \(\eta_i\). The grain distribution parameters chosen by the optimization algorithm will prompt a normal random generator and thereby create a set of Euler angles \((\phi, \theta, \psi)\) for each of the grains. These Euler angles will dictate the coordinate transformation [as given by Eq. (3) in the electromechanical property tensors appearing in the homogenization equations Eqs. (2) - (4)].

Each iteration of the optimization algorithm calls the objective function, the effective piezoelectric coefficient \(d_{ij}^e\). The numerical solution of the coupled piezoelectric problem sought using the FEM would be substituted in the optimization as a function of Euler angles; (a) \(\phi\) and \(\phi\) and (b) \(\theta\) and \(\psi\).

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). In single crystals, the design variables are the three Euler angles \((\phi, \theta, \psi)\) itself. This condition would be enough to scan the entire crystallographic space to search for the enhanced piezoelectricity.

The optimization problem can be summarised as to

\[
E(R_1) \equiv d_{33}(\alpha) \Rightarrow E(R_i) \equiv d_{33}(\sigma_\phi, \mu_\phi, \sigma_\theta, \mu_\theta, \sigma_\psi, \mu_\psi) \quad (7)
\]
strain along the electric field $E$ expressed as $\varepsilon$.

The spontaneous polarization direction of the BaTiO$_3$ coefficient tensor better describes the piezoelectricity along with the optimization. Good agreement between our implementation before starting with the optimization. Nonetheless, the extrinsic contributions associated with the displacement of domain walls at external fields has a profound influence on the dielectric, mechanical and piezoelectric properties of ferroelectric materials. Therefore, the size effect of grains and domains are critical to the piezoelectricity of ferroelectrics as well.

### III. RESULTS AND DISCUSSION

#### A. Objective: single crystal piezoelectricity

Since the $d_{33}$ component (in tensor form $d_{33}$) is expressed as $\varepsilon_{33} = d_{333} E_3$, where $\varepsilon_{33}$ is the piezoelectric strain along the electric field $E_3$ of piezoelectric coefficient tensor better describes the piezoelectricity along the spontaneous polarization direction of the BaTiO$_3$.

We designate it as the objective function for our first optimization problem. First, we would check the robustness of the homogenization implementation before starting with the optimization. Good agreement between our homogenization results on single crystalline BaTiO$_3$ and the experiment by Zgonik et al is as shown in Table I. The comparison on Table I would provide only a check to the correctness of the algorithm. In fact, in our simulation we use the elastic stiffness $C_{\mu\nu}$, piezoelectric stress constants $e_{\mu\nu}$, and clamped dielectric permittivity $\kappa_i^{\text{eff}}$ from the measurements of Zgonik et al. The present simulation is limited in its detail in the sense that we have not accounted the domain structure of the grains since they are assumed to be composed of a single domain. Nonetheless, the extrinsic contributions associated with the displacement of domain walls at external fields has a profound influence on the dielectric, mechanical and piezoelectric properties of ferroelectric materials. Moreover, the size effect of grains and domains are critical to the piezoelectricity of ferroelectrics as well.

![FIG. 3: Variation of effective piezoelectric stress coefficients](image)

The evolution of the objective function $d_{33}$ with the temperature in single crystal BaTiO$_3$ is shown in Fig. 3. The piezoelectric coefficient $d_{33}$ obtained after optimization ($d_{33} = 223.7$ pC/N) compares well with experimental values (also see, Table I) and other theoretical results. The solution $\phi$, $\theta$ and $\psi$ are $-2.182, 0.873$ and $-0.175$ radians respectively. This if expressed in degrees ($\phi = -125^\circ$, $\theta = 50^\circ$ and $\psi = -10^\circ$) would correspond to one of the $<111>$ directions of the BaTiO$_3$ single crystal along which the maximum piezoelectric coefficient of $d_{33} = 203$ pC/N is measured.
TABLE II: Optimized piezoelectric coefficient $d_{33}$ along with experimental values of single crystal and polycrystal BaTiO$_3$.

| Authors       | Optimum objective function, $d_{33}$ (pC/N) | Single crystal | Polycrystal |
|---------------|-------------------------------------------|----------------|-------------|
| Present       | 223.7 $^a$                                | 270.7 $^b$     |
| Wada et al. $^c$ | 203.0                                     | -             |
| Zgonik et al. $^d$ | 90.0                                      | -             |
| Bechmann $^e$  | -                                         | 191.0          |

$^a$Optimization is achieved when the crystal reaches the orientation Euler angles ($\phi = -2.182, \theta = 0.873, \psi = -0.175$). This is a [111] orientation.

$^b$Optimal microstructure is characterised by the orientation distribution parameters ($\mu_0 = 0.785, \sigma_0 = 0.1, \mu_1 = 1.134, \sigma_1 = 3.3, \mu_2 = 0.873, \sigma_2 = 4$).

$^c$Experiment in Ref. 53 for [111]-poled single crystal BaTiO$_3$

$^d$Experiment in Ref. 32 for [001]-poled single crystal BaTiO$_3$

$^e$Experiment in Ref. 58 for poled polycrystalline BaTiO$_3$

The plots on Figs. 2(a) and (b) reveals that the piezoelectric coefficient $d_{33}$ always confined within $\pm 223.7$ pC/N. Here $YZ$-projection (circles) on Figs. 2 (a) and (b) shows peaks at $\theta = \pm 50^\circ$ and at $\pm 140^\circ$. That $d_{33}$ here follows the same pattern shown in earlier studies about the rotation ($\theta$) of the single crystal provides an additional proof of the efficiency of the algorithm and show how comprehensive is the solution space. Also, it can be seen that the $[XZ$-projection (rectangles) on Figs. 2 (a) and (b)] angles $\phi$ and $\psi$ have no visible influence on the piezoelectricity of BaTiO$_3$. The $d_{33}$ exhibits both highs and lows irrespective of the values of $\phi$ and $\psi$ as dictated by the symmetric reduction of the transformation equation in Eq. (11). Also, since the spontaneous polarization in tetragonal BaTiO$_3$ is along the [001] direction, any rotation of that axis of the crystal affects the piezoelectricity of the crystal measured in a local frame of reference. This is evident considering the fact that the Euler angle $\theta$ measures the amount of rotation of the [001] axis of BaTiO$_3$. (This aspect would be discussed in detail in the coming section). In other words, for single crystalline BaTiO$_3$ to display enhanced piezoelectricity, one should cut the single crystal at an angle away from the polar axis.

The objective function $d_{33}$ attains the optimum value of 223.7 pC/N at a temperature of 6.4 [Fig. 11] and at the thirteenth iteration. (We have listed the $d_{33}$ parameter obtained at the optimization in Table 11 along with the experimental values). After the symmetric reduction of the coordinate transformation equation $d_{ij} = \sum_k \mu_k a_{ik} a_{1j} \phi_{mn}$, where $a_{ij}$ are the elements of Euler transformation matrix in Eq. (11), yields

$$d_{33} = (d'_{15} + d'_{31}) \sin^2 \theta \cos \theta + d'_{33} \cos^3 \theta$$ (9)

for tetragonal $4mm$ symmetry of BaTiO$_3$. Here the primed coefficients corresponds to that of the spontaneously polarized BaTiO$_3$. Almost 89% of the contribution to the enhanced $d_{33}$ is from the first term of this equation containing the shear constant $d_{15}$, i.e., while evaluating the terms in the above Eq. (9) we obtain the contribution from the first term as 198.8 pC/N and the rest of 223.7 pC/N is derived from the last term $d_{33} \cos^3 \theta$. We have used the simulation results of $d'_{ij}$ from Table 11 for this calculation. This corroborates the notion of the relation between polarization rotation, shear constant $d_{15}$ and the eventual piezoelectric enhancement.

The tetragonal phase of BaTiO$_3$ has

$$d_{33} = 2e_{31}s_{13} + e_{33}s_{33}$$ (10)

Table 11 provides the set of piezoelectric coefficients $d_{ij}$, $e_{ij}$, and compliance $s_{ij}$ obtained at the point where the $d_{33}$ attains the optimal value in BaTiO$_3$ single crystals. Obviously, the major contribution to the $d_{33}$ comes from the second product of the above equation (Eq. 11). As one can see from Tables 11 and 11 the piezoelectric coefficient $e_{33}$ jumps from 6.7 to 27.3 C/m$^2$. This big increase contributes the major part of the enhancement of $d_{33}$. The variation of $e_{33}$ and $d_{ij}$ are shown in Fig. 3. Fig. 3 facilitates the understanding of the geometrical relations contributing to the enhancements of piezoelectricity in BaTiO$_3$. In addition to this as shown in Eq. 9 $d_{33}$ becomes a linear combination of $d_{ij}$ after coordinate transformation. This aspect would also contributes to the enhancement of $d_{33}$.

B. Objective: polycrystal piezoelectricity

The optimization of polycrystal BaTiO$_3$ is treated in this section. The novelty in the present work is that...
the optimization procedure being applied to the ferroelectrics. Precisely, a stochastic optimization is developed used to find out the best grain configuration which will output a piezoelectric polycrystal wherein the piezoelectricity is maximum compared to the other possible configurations. We analyze the most general case with $(\sigma_\phi, \sigma_\theta, \sigma_\psi) \in [0,5]$ and $(\mu_\phi, \mu_\theta, \mu_\psi) \in [0, \pi/2]$ as given by Eq. [8]. The results are shown in Fig. [4]. The initial and final temperature of the optimization is set to be 1 and 1.0634 $\times 10^{-4}$ respectively. Each step (there would be 42 steps to fall into the final temperature) constitutes 24 iterations as and as a whole the final solution is realized in 1008 iterations. The objective function converges with a value $d_{33} = 270.7$ pC/N which is much higher than both [001] poled and [111] poled single crystal values (see Table [1]). Here, the $d_{33}$ is obviously enhanced by a factor of 3 from the [001] poled single crystal value of $d_{33} \approx 90$ pC/N as is seen in Fig. [4] (Here the $d_{33}$ of textured polycrystal is being compared to that of the [001] poled single crystal). The optimal value of $d_{33}$ is also higher than the corresponding value of an optimally oriented single crystal (where the value was $d_{33} = 223.7$ pC/N as shown in Table [1]). Also this is much higher than the poled polycrystal experimental value of $d_{33} = 191$ pC/N obtained by Bechmann[26].

### TABLE III: Piezoelectric coefficients $d_{j\nu}$ (in PC/N), $e_{j\nu}$ (in C/m$^2$) and compliance $s_{j\mu}$ (in 10$^{-12}$ m$^2$/N) obtained at the point of optimal $d_{33}$ in BaTiO$_3$.

| Phase          | $e_{33}$ | $e_{31}$ | $e_{15}$ | $d_{31}$ | $d_{15}$ | $s_{11}$ | $s_{12}$ | $s_{13}$ | $s_{33}$ | $s_{44}$ |
|----------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Single crystal | 27.3     | -17.7    | 4.7      | -144.2   | 115.4    | 6.7      | -2.5     | -1.4     | 5.9      | 17.9     |
| Polycrystal    | 30.0     | -13.8    | 14.4     | -124.0   | 254.5    | 6.3      | -1.9     | -2.2     | 6.9      | 18.0     |

FIG. 5: Variation of the objective function, the piezoelectric coefficient $d_{33}$ with the design variables, mean and standard deviation of each of the angle distribution in polycrystal BaTiO$_3$. Each of the subplots shows the $d_{33}$ against the design variables, (a) $\mu_\theta$, (b) $\sigma_\theta$, (c) $\mu_\phi$, (d) $\sigma_\phi$, (e) $\mu_\psi$ and (f) $\sigma_\psi$ corresponding to each iteration.

FIG. 6: Variation of the homogenized piezoelectric coefficient $d_{33}$ with the orientation distribution parameters $\sigma_\theta$ and $\mu_\theta$ (in degrees) for the polycrystalline BaTiO$_3$. The other two Euler angles $(\phi, \psi)$ are kept at zero.

The solution obtained is $\mu_\theta = 0.785$, $\sigma_\theta = 0.1$, $\mu_\phi = 1.134$, $\sigma_\phi = 3.3$, $\mu_\psi = 0.873$, $\sigma_\psi = 4$. It means $\theta$s (which measures the canting of the $c$-axis of the crystallographic grain) is kept at a small standard deviation of 0.1 but around a mean value of 0.785 radians ($\approx 45^\circ$). Nevertheless, the other two angles are distributed with larger standard deviations close to the random. Thus the present solution suggests one should keep the Euler angles $\phi$ and $\psi$ related to the orientation of ab-plane of the crystalites to be in random while the orientation $\theta$, of c-axes is kept close to $45^\circ$ but with a marginal standard deviation. A similar kind of result in polycrystalline BaTiO$_3$ was obtained numerically by Garcia et al.[60]. They have shown that maximum piezoelectric response ($d_{33}$ or $d_{31}$) is exhibited by polycrystal ferroelectrics possessing specific crystallographic textures.

The dependence of the spread and shape of the orientation distribution on the piezoelectric properties are displayed in the three-dimensional plots on Figs. [5]. It can be seen that the effective piezoelectric constant $d_{33}$ clearly shows a distinctive dependence on the distribution parameters pertaining to the Euler angle $\theta$ [as can be seen from the pattern shown in Figs. [5] (a) and (b)]. (The contour on the $YZ$-projection on the plots shows the values of $d_{33}$ for the parameters $\mu_\theta$, $\sigma_\theta$, $\mu_\phi$, $\sigma_\phi$, $\mu_\psi$, $\sigma_\psi$). The piezoelectric coefficient follows a specific pattern for both $\mu_\theta$ and $\sigma_\theta$ shown on subplots Figs. [6] (a) and (b) respectively. $d_{33}$ shows peaks around the mean $\mu_\theta \approx 0.7 - 0.8$ radians which would be around $\approx 45^\circ$. 

Also, \(d_{43}\) steadily increases its value as the standard deviation \(\sigma_\theta \to 0\), which is clearly a tendency towards an aligned and textured ceramic material.

Next, we will study the influence of randomness on the enhancement of piezoelectricity in ceramic \(\text{BaTiO}_3\). An important aspect observed in the optimization study is that in polycrystals, unlike in single crystals, the orientation of the ab-plane of the crystallites do play a role in determining its piezoelectricity. Another simulation is done to verify this point as shown in Fig. 6. Here the simulation of the ab-plane of the crystallites do play a role in the optimization study is important. The simulation results in \(d_{33} = 236\) pC/N which is close to that of [111]-oriented single crystal. This would further point out that c-axes of the crystallites should be constrained to have a specific orientation while the ab-plane need not be kept at a specific texture but at random. This condition will deliver a ceramic piezoelectric material possessing better piezoelectricity than any other phase (optimally oriented single crystal or ceramic). Hence randomness in the orientation of grains, if utilized judiciously, could be useful for manufacturing piezoelectric ceramics which outperform single crystals. Another point to noted here is the role played by the shear constant \(d_{15}\) in the enhancement of \(d_{33}\). Here the analysis of the shear constant in the enhancement of piezoelectric response is complicated because of the presence of grain boundaries in polycrystal FEs. Yet, it would be important to know the value of \(d_{15}\) to shed light on the origin of piezoelectric enhancement. The value of the shear constant obtained at the maximum of \(d_{33}\) is \(d_{15} = 254.5\) pC/N (see Table III). As in single crystals the enhancement in \(d_{33}\) in polycrystals is accompanied by a sizeable \(d_{15}\) value in \(\text{BaTiO}_3\). A similar conclusion was drawn by Garcia et al., where they show that in partially textured ceramics with a \(d_{15}\) larger than \(d_{33}\) is a good choice for enhancement of polycrystal \(d_{33}\).

The optimal orientation distribution across the six faces of the microstructure (representative volume element) is shown in Fig. 7. Since the angle \(\theta\) influences the \(d_{33}\), the most, that only is shown. It is seen that (Fig. 7) the angles are mostly clustered around 0.8 radians (\(\approx 45^\circ\)). The effective piezoelectric coefficient is dictated by the transformation of coordinates involving the Euler angles (see Eqs. 1 and 5) and hence is influenced by the rigorous combinations provided by the randomness. One of the possible reasons for higher piezoelectricity in FE ceramics with a certain pattern of grain distribution is the role played by the intrinsic polarization of the grains. The misalignment of the polarization in the neighboring grains would impart residual stresses, which couples with the electrical field to enhance the polarization and thereby the piezoelectricity. In the optimal distribution, the polarizations of the juxtaposed grains are configured in such a way that they will contribute positively to the overall increase of piezoelectricity of the polycrystal.

In summary, we have introduced a global optimization technique to identify the ideal configuration of both single and polycrystal FE. This method can be used to the FEs of any symmetry and to any objective function involving electromechanical coefficients. Here this method is applied to the perovskite, tetragonal ferroelectric \(\text{BaTiO}_3\). The paper predicts configuration of crystallites which maximizes the piezoelectricity of the polycrystalline ferroelectrics. The orientation distribution resulted from electrical and mechanical poling is limited by many factors. The alignment of domains with the poling field is by switching its polarization to an equilibrium position defined by the symmetry. The as-grown polycrystal before poling has domains randomly oriented. Thus the poling doesn’t yield the polarization vectors (of domains) all aligned along the field since there may not exist an equilibrium orientation for some domains along the poling field direction. Apart from being provide a guide to experiment, essentially it doesn’t suggest a particular method (for instance, mechanical or electrical poling, tape-casting, templated grain growth, hot forging etc.) to realise the predicted crystallite configuration. A plausible approach is to adopt a combination of suitable processing method (to achieve a certain degree of preferred orientation in the unpoled state) and poling.

In this work, we have observed significantly enhanced piezoelectric response in ferroelectric polycrystals at certain grain configurations. In single crystal \(\text{BaTiO}_3\) the piezoelectricity is found to be larger along a nonpolar direction away from the polar axis. We have optimized the
ferroelectric ceramic by design at the microstructure level for piezoelectric applications. The solution obtained from the optimization procedure results in a three-fold enhancement of piezoelectricity in the ceramic phase compared to the single crystalline phase. If we use the randomness of the grain orientations judiciously the ceramic can replace even the oriented single crystals in piezoelectricity. A plausible reason behind the anisotropy shown by both rotated single crystal and polycrystal FE could be the macroscopic symmetry. The crystallographic symmetry is characterised by the anisotropic (or isotropic) physical properties. The product phase obtained after the crystal orientation might be different from the parent phase in symmetry. The insight obtained from the optimization have the potential to advance the design and discovery of complex FE configurations with superior piezoelectric performance. Further studies in this direction in relaxor ferroelectrics, where the single crystals display larger piezoelectricity, could inaugurate new possibilities in technological applications which involves the requirement of high piezoelectricity.

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