NONLINEAR MODELING OF
HIGH FIELD FERROELECTRIC CERAMICS FOR
STRUCTURAL ACTUATION

by

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Abstract

This thesis investigated the behavior of ferroelectric ceramics under high field and stress. First, both low and high field characterization tests were done to quantify the material behavior. In the low field tests, resonant tests were used to measure the material constants. High field tests were carried out to study the extensional characteristics of sandwich structures, which illustrated the behavior of the material under high field and stress. A model describing the nonlinear behavior of polycrystalline ferroelectrics during polarization reversal was then proposed. The model is based on a description of the polarization reversal behavior of a single piezoelectric crystallite in the ceramic. The polarization of the single crystallite can be switched among the six allowable directions in the lattice if work done by the external electrical and/or mechanical loads exceeds internal energy barriers. The ceramic is then modeled as an aggregate of these crystallites rotated into random orientations. Two methods were developed to calculate the ceramic responses from the crystallite responses. The first method calculates the ceramic responses by the averaging of crystallite responses in global coordinates. The second method uses a set of series expansions that depends on the net alignment of the crystallites to arrive at the ceramic response. Finally, the results of model simulations for the clamped PZT wafers in the sandwich structures were compared with the experimental data. Comparisons on the overall quality of the model prediction as well as quantitative comparisons of specific material constants were carried out.
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Nomenclature

\( c^a \) - Elongation ratio of the lattice
\( c^{CE} \) - Stiffness matrix of crystallite under constant electric field
\( c^{D} \) - Elastic stiffness under constant electrical displacement
\( c^{E} \) - Elastic stiffness under constant field
\( c^{m} \) - Stiffness matrix of matrix material
\( C \) - Curie-Weiss constant
\( C_o \) - Shunting capacitance of the piezoelectric equivalent circuit
\( C_i \) - Serial capacitance of the piezoelectric equivalent circuit
\( d \) - piezoelectric coefficient in series expansion method
\( d_{ij} \) - Piezoelectric strain constants
\( \tilde{d}_{ij} \) - Rotated crystallite piezoelectric constant matrix
\( D \) - Electrical displacement
\( D^* \) - Electrical displacement associated with crystallite polarization
\( D_{i}^{\text{total}} \) - Total electrical displacement in crystallite
\( D_{i}^{\text{diele}} \) - Electrical displacement in crystallite due to electric field
\( D_{i}^{\text{piezo}} \) - Electrical displacement in crystallite due to piezoelectricity
\( D_{i}^{\text{spont}} \) - Electrical displacement in crystallite due to spontaneous polarization
\( e_{ij} \) - Piezoelectric stress constants
\( E \) - Electric field
\( E_c \) - Coercive field
\( f_m \) - Frequency at which the piezoelectric vibrator has minimum impedance
\( f_{mr} \) - Frequency at which the transmission circuit has maximum transmission
\( f_n \) - Frequency at which the piezoelectric vibrator has maximum impedance
\( f_p \) - Parallel (lossless) resonance frequency
\( f_s \) - Motional (series) resonance frequency
\( G \) - Gibbs free energy
\( G_i \) - Elastic Gibbs energy
\( H_i \) - Helmholtz free energy
\( i_{\text{max}} \) - Maximum switching current
\( M \) - Figure of merit
\( N \) - Net alignment of polarization on poling axis
\( P \) - Polarization
\( P_r \) - Remanent polarization
\( P_s \) - Spontaneous polarization
\( Q \) - Electrostriction coefficient, quality factor
\( r \) - Capacitance ratio \( \left( \frac{C_o}{C_i} \right) \)
\( R^e \) - Rotation matrix for electric field and displacement
\( R^t, R^s \) - Rotation matrix for stresses and strains in Voigt notation
\( s^E \) - Elastic compliance of crystallite under constant field
\( s^D \) - Elastic compliance under constant electrical displacement
\( s^E \) - Elastic compliance under constant field
\( s^E \) - Rotated crystallite compliance
\( s^N \), \( s^l \) - compliance coefficients in series expansion method
\( S^* \) - Strain associated with crystallite polarization
\( S_i \) - Strain
\( S^\theta(\Theta) \) - Normal thermal expansion
\( S_s \) - Spontaneous strain
\( S_{ij}^{\text{total}} \) - Total strain in crystallite
\( S_{ij}^{\text{mech}} \) - Strain in crystallite due to mechanical stresses
\( S_{ij}^{\text{piezo}} \) - Strain in crystallite due to piezoelectricity
\( S_{ij}^{\text{spont}} \) - Strain in crystallite due to spontaneous polarization
\( t \) - Thickness
\( t_s \) - Switching time
\( T_i \) - Stress
\( U \) - Internal energy, energy barriers
\( W^{\text{switch}} \) - Work done by external load in switching spontaneous polarization
\( \alpha \) - Activation field, rate function in internal variable model
\( \beta, \gamma, \delta \) - Coefficients in Devonshire’s phenomenological model
\( \varepsilon_0 \) - Dielectric permittivity of free space
\( \varepsilon \) - Dielectric permittivity
\( \tilde{\varepsilon}^T \) - Rotated crystallite dielectric permittivity matrix
\( \theta, \phi, \psi \) - Angular variables in spherical coordinates
\( \psi \) - relative stiffness of a sandwich structure, \( \frac{c_x A_x}{c_p A_p} \)
\( \Theta \) - Temperature
\( \Theta_o \) - Curie-Weiss temperature
\( \Theta_c \) - Curie point
\( \nu \) - Poisson’s Ratio
\( \Pi \) - Total potential energy
\( \rho \) - Charge density
\( \sigma \) - Specific entropy
\( \chi \) - Susceptibility
Chapter 1 : Introduction

The recent developments in the area of adaptive structures have revolutionized the traditional role of structures. Typically structures that can be classified as adaptive incorporate actuators, sensors, and some control systems that directly influence the structural behaviors. Thus, this kind of structural components can directly improve system performance in addition to provide support for other components in the system. There are many applications of adaptive structures. One of the first applications of such ideas are active damping and isolation in large structures. In these applications, knowledge of the dynamic behaviors of the structures is typically used to tailor a suite of actuators and sensors to minimize the effects of external disturbance on the structure [1]. Recently, other applications of adaptive structures have been developed. One example is adaptive optics, which applies the principle of adaptive structures to optical systems. Deformable mirrors with various kinds of actuators were constructed to automatically compensate atmospheric distortions and deformations due to thermal gradient [2]. In the area of aerodynamics, solid state actuators have been used to directly bend and twist an active wing [3]. This has provided degrees of freedom in controlling the aerodynamic characteristics of the wing, such as flutter speed, that were never possible before with flaps and ailerons. In all these applications, the constraints imposed by the requirements on overall weight, available space, and actuation authority limit the choices of actuators. Traditional means of actuation such as electromechanical motors, hydraulic and pneumatic systems often fail to satisfy all the criteria. In many cases, actuation by means of active materials is the most suitable, if not the only, alternative to achieve the required performance.

There are many advantages in using actuators made of active materials. They are usually compact and lightweight compared to conventional motors and hydraulic systems. The responses of these solid state actuators are extremely fast, thus increasing the overall system performance. There are many types of active materials in use. Examples of commonly used materials are piezoceramics, electrostrictives, and magnetostrictives. There are other more exotic materials in development, such as shape memory ceramics, that promise much higher actuation authority as well as new actuation capabilities. These materials share some essential characteristics that make them extremely suitable for actuation needs. All these materials are in either alloy or ceramic form, which enable actuators of different shapes and sizes to be manufactured easily. All of them have rather high mechanical moduli that enable an efficient transfer of strain energy from the actuator to the host structure. All of them can directly convert electrical energy into strain energy without additional mechanisms, thus decreasing the complexity of the system. Besides
these similarities, the various materials behave very differently and each addresses unique requirements under different circumstances.

Piezoceramics are perhaps the most commonly used active material in actuators of adaptive structures. Piezoceramics are available in the form of either raw ceramics or packaged actuators. They have been used extensively in hydrophone and ultrasonic applications. Thus, many aspects of their behaviors are quite well understood. However, their nonlinearities in electromechanical coupling properties and hysteretic nature have limited structural applications to a small operation range where linear material properties can be approximated. In reality, only ferroelectrics, a subclass of piezoelectrics, are used for actuation purposes. Unlike other piezoelectrics, which have non-polar lattice structures, ferroelectrics exhibit a spontaneous polarization which can be oriented in at least two crystallographic directions even when an electric field is not present. Spontaneous polarization within the material can be switched among these directions by applying an electric field. The presence of a non-vanishing, switchable polarization in ferroelectrics lends them flexibility in applications. Apart from availability, the performance and reliability of ferroelectrics are well established due to the long history of applications. In addition, ferroelectric material properties are much less sensitive to temperature changes than those of electrostrictives.

Ferroelectrics also have some inherent disadvantages. Ferroelectrics behave in a rather nonlinear fashion under high field and stress conditions; there is also significant hysteresis in ferroelectrics as compared to other active materials. These nonlinearities are fundamentally due to the switching of spontaneous polarization in the material. A list of other nonidealities is well documented in Chapter 2 of Reference 4. In spite of these undesirable qualities, ferroelectrics are still the chosen material in many applications.

As the demand for higher structural actuation authority continues to grow, however, the required applied electric field levels for ferroelectric actuators must also increase beyond the linear régime. Under such operating conditions, hysteresis and other nonlinear behaviors due to polarization reversal in ferroelectrics can no longer be ignored. Predictions of system behavior using the linear material model completely break down in the presence of such nonlinear effects. In some cases, the nonlinear strain–field relation can be overcome by curve-fitting the exact material behavior. However, there are further complications introduced by hysteresis; the electromechanical properties depend intimately on the history of material states. Thus, it is extremely difficult to predict the material behavior at any given time for an arbitrary history of applied field with a curve-fitted model. In some dynamic applications, such as vibration problems, where the applied field is relatively low (not high enough to cause large scale polarization reversal), charge control,
instead of voltage control, can be used to eliminate most of the hysteresis observed in the material [4]. However, in quasi-static applications, such as shape control, there is no way to circumvent the problems caused by hysteresis with a linear or curve-fitted material model.

An even more serious problem that challenges the usefulness of the linear model is the dependence of material states on the strain of the ferroelectrics. It was discovered that the amount of actuation strain created in ferroelectric actuators is highly dependent on the total strain of the material [4]. Thus, the prediction of induced strain in the structure based on the free strain of the actuator is no long valid. For low field applications, an ad hoc method that changes the piezoelectric constant is available to improve the model predictions [4]. However, as higher electric fields are applied on the actuator, induced stresses in the actuators also increases, and this problem becomes much more serious. This effect combined with the failure of the linear model at high field completely rule out any possibilities that an adequate solution can be obtained by modifying the linear model. A nonlinear model that fundamentally describes the processes in the material is needed to tackle such problems.

Besides the above issues in direct applications of high field ferroelectric actuators, there are other problems encountered in manufacturing and analyzing newer ferroelectric actuators whose solutions must rely on a nonlinear ferroelectric model. In the manufacturing process of all ferroelectric actuator, a process called poling must be applied to activate the electromechanical coupling of the material. During poling, a large electric field is applied to polarize the material. Such a process is highly nonlinear in nature, and the nonlinear processes which occur during poling are exactly the cause of the nonlinearities described previously. For actuators with simple geometries, such as plates and disks, both the electric field and the polarization field in the material are approximately uniform. In these cases, the uniformity assumption enables simple empirical relations to be used in predicting the outcome of such processes.

However, as newer actuators such as piezoelectric fiber composite [5] and plate actuators with interdigitated electrodes [6] are developed to realize higher level of actuation strain and anisotropic actuation capabilities, empirical methods are no longer sufficient. In these designs, both the electric field and the polarization in the material are no longer uniform. A more sophisticated analysis for predicting the outcome of the poling processes is required. Furthermore, more complex actuators also incorporate more choices to be made during the design process. Without an adequate nonlinear model, it is very difficult to have realistic evaluations in the tradeoff of different designs.

Beyond the application of ferroelectrics in actuation, there is another far-reaching consequence in obtaining an effective nonlinear material model. For all the active materials
that are potential choices for actuators, existence of electromechanical coupling is the primary requirement. Invariably, manipulation of polarization in materials remains the prime mechanism in transferring electrical energy into mechanical energy. Materials that provide large actuation strains usually have dramatic changes in polarization, and also highly nonlinear material behaviors. Construction of a good framework in describing polarization in material holds the key for harnessing the enormous potential for actuation by polarization control in ferroelectrics, as well as in other materials.

There are two objectives in this work. First, postulate a nonlinear model to capture the behaviors of polarization in a ferroelectric ceramic. The model will be able to predict polarization reversal, hysteresis, and the effects of stresses on the material behavior. This will enable modeling of ferroelectrics used as high authority actuators, operating under high field and stress. Second, provide a general framework for modeling new types of active materials (e.g., shape memory ceramics) which display similar nonlinearities.

1.1 BACKGROUND ON FERROELECTRICITY

The characteristic of ferroelectrics that permits structural actuation is the presence of an electromechanical coupling, loosely referred to as *piezoelectricity*, which enables the exchange of electrical and mechanical energy. Strictly speaking, piezoelectricity is the ability of a material to produce charges linearly proportional to the mechanical stress applied to the material. The inverse piezoelectric effect is then the ability to produce mechanical strain that is proportional to the applied charge. The presence of such characteristics depends entirely on the lattice structure of the material.
As illustrated in Figure 1-1, all the crystalline materials can be classified into 32 point groups according to their lattice structures. A point group is a classification of crystalline structures by the type of symmetry exhibited in the microscopic structures such as rotation axis and reflection mirror. Among all 32 point groups, only 21 have non-centrosymmetric structures; of these, all but one display the piezoelectric effect. Thus, it is obvious that asymmetry in the lattice structure is a prerequisite for the existence of piezoelectricity. Among these 20 point groups, ten belong to a subgroup known as pyroelectrics. Pyroelectrics are polar materials that have a unique polar axis. They exhibit a temperature dependent spontaneous polarization along a single polar direction. Ferroelectrics belongs to a subgroup of pyroelectrics, in which the spontaneous polarization can exist in two or more directions. These directions are essentially identical states and polarization can be switched among them by applying an external field. This is the type of material that are used in actuators. According to the crystal—chemical classification, there are two groups of ferroelectric crystals. The first one is the hydrogen bond type crystals, such as potassium dihydrogen phosphate (KDP) and Rochelle salt. The other is the double oxide type crystals, such as barium titanate and potassium niobate [7, p.11]. Crystals are generally used in studying physical properties of different compositions, especially the microscopic behaviors of the lattice. However, crystals are unsuitable for engineering applications due to difficulties in manufacturing and shaping crystals into desired shapes. Thus ferroelectric ceramics are typically use, especially barium titanate and lead zirconate titanate (PZT). In commercial production, compositions are sometimes doped with a small
amount of other elements, such as barium or niobium to fine tune certain characteristics of the ceramics for specific applications.

A large constant electric field is applied to newly produced ferroelectrics to align the dipole moments inside the material, which are initially oriented in arbitrary directions. This procedure is called poling\(^1\). In ceramics, a uniform spontaneous polarization cannot be achieved due to the polycrystalline structure. Nonetheless, poling will leave a remanent polarization in the ceramic. Usually the material will be left to age for some time after poling to let the material properties settle down to steady state values. Ferroelectrics in general, regardless of crystal or ceramic, have three very important properties: ferroelectric phase transition, polarization reversal, and the existence of domain structures. These properties, along with the existence of electromechanical coupling, material nonlinealities, and memory effects, stem from one single source — spontaneous polarization. The following sections will explore the dependence of various material behaviors on spontaneous polarization in ferroelectrics.

### 1.1.1 Ferroelectric Phase Transitions

The presence of ferroelectricity in a material is characterized by the existence of reorientable spontaneous polarization. Most of the ferroelectrics only display such phenomenon in a specific range of temperatures. When the material is below a temperature called the Curie point, the material behaves like ferroelectrics. Above the Curie point, the material is in the paraelectric phase in which it possesses no spontaneous polarization. As the temperature of a ferroelectric is reduced below the Curie point, it undergoes a phase transition which involves distortions of the crystal lattice. Usually, the lattice structure in the paraelectric phase has a higher symmetry than its ferroelectric counterpart [8, p.11]. For example, barium titanate has a Curie point at 120°C and changes from a cubic to a tetragonal structure as the temperature decreases. In the special case of Rochelle salt, however, has a lower Curie point at -18°C in addition to the higher Curie point at 24°C; the ferroelectric phase only exists between these two temperatures [9]. Some crystals such as guanidine aluminum sulfate hexahydrate (GASH) remain ferroelectric even at the decomposition temperature and thus does not have a Curie point [10].

\(^1\) Most commonly used ceramics, like barium titanate and PZT, do not exhibit the piezoelectric effect before poling. The reason is that in the virgin state, all domains are randomly oriented and the piezoelectric contribution of each domain is averaged out. Thus poling provides some order to the domain structure and resulting in a net piezoelectricity.
Besides the absence of spontaneous polarization, the paraelectric phase is also characterized by the behavior of its dielectric permittivity near the Curie point. When the lattice structure undergoes distortions around the Curie point, all the macroscopic properties display large and sudden changes with respect to the variation of temperature, usually referred to as anomalies. The dielectric permittivity however, can be simply described by Curie–Weiss law,

$$\varepsilon = \varepsilon_o + \frac{C}{\Theta - \Theta_o}, \quad (\Theta > \Theta_o)$$

(1.1)

where $\varepsilon_o$ is the temperature independent permittivity of the material when far away from $\Theta_o$, $C$ is the Curie-Weiss constant, and $\Theta_o$ is the Curie–Weiss temperature. In general, $\Theta_o$ is lower than the Curie point, except in some special cases, $\Theta_o$ is equal to the Curie point. Although spontaneous polarization vanishes in the paraelectric phase, piezoelectricity does not necessarily disappear. For crystals lattices with lower symmetry in the paraelectric phase, significant piezoelectricity can still exist, potassium dihydrogen phosphate (KDP) is one example. In the ferroelectric phase, its piezoelectric effect is strengthened by the existence of spontaneous polarization [11, p.44]. As for other crystals with perovskite-type structures like barium titanate and lead zirconate titanate (PZT), as shown in Figure 1-2, piezoelectricity only exists in the ferroelectric phase where electrostriction in the crystal is amplified by the presence of spontaneous polarization [12, p.219]. Since the spontaneous polarization decreases as temperature increases, the temperature of the material is usually raised during the poling process, so that a lower electric field can be used.

![Figure 1-2. The lattice structure of barium titanate (a) the above the Curie point, and (b) below the Curie point. [8, p.3]](image)

There are two types of paraelectric–ferroelectric phase transitions, namely first and second order transitions. In both cases, as temperature decreases, spontaneous polarization increases monotonically below the Curie point and saturates at low temperature. The major
difference is the behavior of the spontaneous polarization at Curie point. In materials with second order transition, spontaneous polarization vanishes in a continuous manner at Curie point. Materials with this type of phase transition have the Curie–Weiss temperature equal to the Curie point. Triglycine sulfate (TGS) is one such material.

For materials with first order transitions, spontaneous polarization vanishes in a discontinuous manner at the Curie point. As a result, all the macroscopic parameters that are effected by the presence of spontaneous polarization in the ferroelectric phase will have a jump at the Curie point. In addition, when the temperature is close to the Curie point, a metastable state with no spontaneous polarization can be induced in the ferroelectric phase by applying appropriate external influences, such as an electric field. Likewise, a metastable state with spontaneous polarization can be induced in the paraelectric phase when the temperature is at or slightly higher than Curie point [13, p.77]. Barium titanate, like most of the ferroelectrics has first order transition [13, p.76].

1.1.2 Polarization Reversal

Polarization reversal is a unique feature that distinguishes ferroelectrics from other pyroelectrics. Ferroelectricity is named for ferromagnetism since the dielectric behavior of the former during reversal is similar to the magnetic behavior of the latter. Figure 1-3 illustrates the typical relation between \( D \), the electrical displacement which is related to the polarization by \( \vec{D} = \varepsilon_o \vec{E} + \vec{P} \) and \( E \), and the electric field. Electrical displacement is often measured instead of polarization because of the difficulties involved in the direct observation of polarization.
Figure 1-3. Typical relation between electric field \( (E) \) and electrical displacement \( (D) \) for a ferroelectric material. [8, p.10]

The relation between \( D \) and \( E \) is multiple-valued and depends on the complete past time history of both variables. The illustration in Figure 1-3 is known as the hysteresis loop. When the ferroelectric has no net polarization at \( O \), it is in the virgin state. When the electric field increases, the state of the material follows the path ABC and approaches the saturation of the polarization. If the path BC is extrapolated back to the intercept at E, the corresponding value of electrical displacement \( P_s \) is the spontaneous polarization. As the electric field starts to decrease to a minimum following the path CBDFG, the material retains non-zero electrical displacement \( P_r \) at D, which is known as the remanent polarization when the electric field vanishes. This is the net polarization observed in the bulk material. The electrical displacement finally vanishes as the field reaches \( E_c \) at \( F \). \( E_c \) is the coercive field. It is usually not a well-defined quantity for a bulk material and it will vary with the temperature, frequency, and waveform of the applied electric field [11, p.7]. When the field increases again, the loop is completed through the path GHBC and it does not return to the origin. When the material is in its virgin state, its dielectric permittivity is given by the slope of the initial curve OA close to the origin. The slope of the hysteresis loop around D is the small field dielectric permittivity of the ferroelectric in the polarized state.

Since ferroelectrics have the piezoelectric property, a similar hysteresis between electric field and strain can be observed. This behavior is the direct consequence of the hysteresis present in the polarization since piezoelectricity in ferroelectrics is largely (in many cases solely) due to the presence of spontaneous polarization. The field–strain
hysteresis loop is known as the butterfly loop due to its shape (Figure 1-4). The nonvanishing strain at zero field is known as the remanent strain, which depends on the remanent polarization. The slope of the loop at the remanent strain is the piezoelectric strain constant.

Figure 1-4. A typical butterfly loop of a ferroelectric

As mentioned in the above section, spontaneous polarization changes with temperature. Thus the shape of the hysteresis loop also changes with temperature. As shown in Figure 1-5, when the temperature increases, spontaneous polarization decreases and so does the area enclosed by the hysteresis loop. The loop becomes a single-valued curve beyond the Curie point. The manner in which the loop vanishes will depend on the type of transition that is involved. In addition, the hysteresis loop also depends on the external stress on the material and the direction of loading, as illustrated in Figure 1-6. As seen in Figure 1-6 (a), mechanical stress applied perpendicular to the direction of the electric field (which is the same as the direction of the polarization) does not drastically affect the size of the hysteresis loop. However, when compressive stress is applied against the direction of the polarization, as shown in Figure 1-6 (b), the total amount of polarization achieved in the ferroelectric is greatly decreased.

Figure 1-5. Effects of temperature on the hysteresis loop. [14]
1.1.3 Ferroelectric Domain Structures

On a microscopic scale, the existence of spontaneous polarization and its reversal can be explained by the formation of ferroelectric domains and domain wall movements. Thus, the study of polarization reversal is often called the study of the dynamic properties of domain walls. A ferroelectric domain is a region in the bulk material where the crystal lattice has a uniform polarization. In the absence of an external field or stress, the value of polarization in one domain is the spontaneous polarization. The interfaces between domains are domain walls, which are usually a few unit cells in thickness. Domain walls are classified by the angle between the polarization of the adjacent domains. For two domains that have antiparallel polarization, the domain wall is said to be a 180° domain wall, whereas the wall between two domains that have perpendicular polarization is a 90° domain wall (Figure 1-7). The number of types of domain wall are determined by the crystal structure. In tetragonal structures, 90° and 180° domain walls are allowed while 71°/109° and 180° are allowed in rhombohedral structures. For some materials which have multiple ferroelectric phases, such as barium titanate, the domain structure in the material can change drastically as the temperature changes and the material goes through various ferroelectric-ferroelectric phase transitions. There are many methods that enable direct or indirect observation of domain structures and there is a rather complete list of techniques in Chapter 4 of Reference 10.
Figure 1-7. Typical arrangement of ferroelectric domains and 180° and 90° domain wall in a barium titanate crystal with tetragonal lattice structure.

From a macroscopic point of view, formation of domain structures minimizes the free energy of the crystal [8, p.7]. When the ferroelectric is cooled through the Curie point, domains form randomly, and usually result in very little or no net polarization or piezoelectricity in the bulk material. This is the virgin state of the ferroelectric. When an electric field is applied to the ferroelectric, the polarization in the domains tends to be more aligned with the field. The mechanism that explains such phenomenon is that the external field initiates movements of the domain walls and nucleation of new domains, decreasing the volume of domains that are not in the direction of the field. When the applied field is small, such movements are reversible. However, when the field is increased past the coercive field, some of the domains are switched permanently. Thus, when the field is removed, there is net polarization remaining, as seen in the hysteresis loop. This is referred to as the remanent polarization.

One way of studying polarization reversal is by observing the transient response of the ferroelectric crystals after applying pulses of electric field. A series of electrical pulses with alternating polarity is applied to the sample. The duration of the pulse is such that it is long enough for the ferroelectric to reverse the polarization from one direction to the opposite direction. The intervals between pulses should also be long enough for the crystal to reach equilibrium [7, p.51]. The significant measurements in this type of studies are the switching time and the maximum switching current.

The first investigation was carried out on barium titanate by Merz in the 1 to 15 kV/cm range [16]. The data on switching time and maximum switching current was fitted using the following empirical relations,

\[
\begin{align*}
    i_{\text{max}} &= i_o e^{(-\alpha/E)}, \\
    t_s &= t_o e^{(\alpha/E)}. 
\end{align*}
\]

(1.2)

The quantity \( \alpha \) is usually called the activation field and \( t_o \) is a constant. One implication of (1.2) is that even if a small electric field is applied to the crystal, the
polarization is going to reverse when given enough time [11, p.203]. Thus, in the most general sense, the quantity of coercive field is not well defined in barium titanate, or in most other ferroelectrics. Further investigation in the high field region from 10 to 100 kV/cm was done by Stadler [17]. He found that the exponential law of (1.2) should be replaced by the power law at high fields,

$$t_r = kE^{-n},$$  \hspace{1cm} (1.3)

where $k$ is a constant and $n$ is about 1.5. The switching laws (1.2) and (1.3) were also derived by Hayashi based on the kinetics of nucleation and growth of domain walls under various field levels [18].

It is important to note that mechanical stress placed on ferroelectrics can also cause polarization reversal. The nature of reversal due to stress is quite dissimilar to the electrical case. In the case of barium titanate, reversals initiated by electric field tend to align both antiparallel and perpendicular domains to the field direction. Therefore both $90^\circ$ and $180^\circ$ domains are switched. During switching, there are dimensional changes in the sample due to the reorientation of the $90^\circ$ domains. In the case of stress induced reversal, mechanical deformation due to mechanical stress can only reverse $90^\circ$ domains but not $180^\circ$ domains [19]. However, there has been very little investigation on stress induced reversals in ferroelectrics. One of the few related studies was carried out by Cao and Evans [20] on plastic deformation of ferroelectric ceramics under stress because of the partial reversal of ferroelectric domains. This phenomenon can become very important when high field ferroelectrics are used for structural actuation since the stress imposed on the actuators can lower the field level at which sudden reversal will occur.

1.2 A SURVEY OF MODELING TECHNIQUES AND MODELS

In the domain of solid state physics, there are two major approaches to modeling ferroelectricity. The first one is microscopic modeling; to approach the problem from the most fundamental principles of quantum mechanics. The second one is macroscopic modeling, also known as phenomenology, which discards all the underlying ionic interactions and formulates theories based on macroscopic parameters. Each approach has strengths and shortcomings, and the choice of model depends on the nature of the application.

Microscopic models are used primarily to investigate the origins of ferroelectricity and the mechanics of phase transitions in different crystals. Models of this type focus on the dynamic long and short range interactions of ions and electrons in the lattice. Due to the
complexity and number of ions that are involved, this approach is only possible for crystals. There are numerous models formulated from this approach. The first model of this kind was formulated by Cauchy in an attempt to explain piezoelectricity [21]. One of the most important concepts in modern studies of ferroelectricity is the soft mode in the context of lattice dynamics. Soft mode basically describes the instability of a transverse vibrational mode as the cause of ferroelectricity in barium titanate. Detail developments of such models and their generalizations to other materials can be found in Reference 22 to 29. Besides studies on the fundamental origin of ferroelectricity, there were also work in relating microscopic parameters to macroscopic parameters [30-33].

1.2.1 Linear Phenomenological Theory

Although the linear model for ferroelectric is unable to capture many of the important characteristics, its development illustrates the fundamentals of phenomenology, and served as the ground work of many nonlinear models. Thus, it is worthwhile to understand its derivation before attempting to formulate any nonlinear models. This linear phenomenological theory describes the static dielectric, elastic, and thermal properties of a homogeneous material. The following derivation will employ the Einstein summation convention for simplicity. The system is assumed to be an isolated system with a homogeneous dielectric and a conductor in thermodynamic equilibrium. The states of the system can be fully specified by the electrical displacement and electric field $D_i$ and $E_i$, which are defined in all space, and by the displacement field, the stress field, the absolute temperature, and the specific entropy $u_i, T_i, \Theta$, and $\sigma$ which are defined only in the dielectric. $D_i, E_i, u_i$ and $T_i$ are assumed to be sufficiently small and there exists a state at which all four of them vanish simultaneously at some temperature $\Theta_i$, so that linearity relations can be approximated. The strain in the bulk material is defined as,

$$S_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}), \quad (1.4)$$

which should also be small and uniform throughout the dielectric. With these field variables, the first law of thermodynamics with internal energy can be written as,

$$dU = \left(\frac{\partial U}{\partial S_{ij}}\right)_{D_i, \sigma} dS_{ij} + \left(\frac{\partial U}{\partial D_k}\right)_{S, \sigma} dD_k + \left(\frac{\partial U}{\partial \sigma}\right)_{S, D} d\sigma,$$

$$= T_{ij} dS_{ij} + E_k dD_k + \Theta d\sigma. \quad (1.5)$$

---

2 From Chapter 3 of Reference 12
The three pairs of fields \((S_y, T_y), (D_k, E_k),\) and \((\sigma, \Theta)\) are conjugate variables, of which \(S_y, D_k,\) and \(\sigma\) serve as the independent variables of the internal energy. If other combinations of independent variables are desired, a Legendre transformation can be carried out on any pair of conjugate variables to obtain a new thermodynamic potential. In this derivation, the Helmholtz free energy is considered. It is given by

\[
H = U - \Theta \sigma \\
dH = T_y dS_y + E_k dD_k - \sigma d\Theta
\]  

(1.6)

For a system to be in equilibrium, the variation of the potential has to vanish, i.e., \(dH = 0\).

\[
dH = \left(\frac{\partial H}{\partial S_y}\right)_{\Theta, D} dS_y + \left(\frac{\partial H}{\partial D_k}\right)_{S, \Theta} dD_k + \left(\frac{\partial H}{\partial \Theta}\right)_{D, S} d\Theta = 0.
\]  

(1.7)

Assuming the coefficient of each independent variable vanishes independently, the variations of each independent variable in (1.6) and (1.7) can be equated. Thus, the equations of states are

\[
T_y = \left(\frac{\partial H}{\partial S_y}\right)_{\Theta, D}, \quad E_k = \left(\frac{\partial H}{\partial D_k}\right)_{S, \Theta}, \quad \sigma = -\left(\frac{\partial H}{\partial \Theta}\right)_{D, S}.
\]  

(1.8)

Assuming small fields, the equations of states can be linearized about an equilibrium.

\[
T_y = c^{D,\Theta}_{ijkl} S_{kl} - h^\Theta_{mn} D_n + \left(\frac{\partial T_y}{\partial \Theta}\right)_D \Theta,
\]

\[
E_m = -h^\Theta_{mkl} S_{kl} + \beta^{S,\Theta}_{mn} D_n + \left(\frac{\partial E_m}{\partial \Theta}\right)_S \Theta,
\]

\[
\sigma = \left(\frac{\partial \sigma}{\partial S_{kl}}\right)_D S_{kl} + \left(\frac{\partial \sigma}{\partial D_n}\right)_S D_n + \sigma^{S, D} \Theta,
\]

where \(c^{D,\Theta}_{ijkl}\) is the isothermal open circuit stiffness, \(\beta^{S,\Theta}_{mn}\) is the isothermal permittivity at constant strain, \(h^\Theta_{mn}\) is the isothermal piezoelectric stress coefficient, and \((\%)\sigma^{S, D}\) is the specific heat at constant strain and open circuit, where \(\rho\) is the density of the dielectric.

\[
\left(\frac{\partial T_y}{\partial \Theta}\right)_D \text{ is the product of } c^{D, \Theta}_{ijkl} \text{ and the tensor of coefficient of thermal expansion, and } \left(\frac{\partial E_m}{\partial \Theta}\right)_S \text{ is related to the pyroelectric coefficients. This set of equations is very often cast into a matrix form by using Voigt notation in the stress–strain relation. The relations between the six thermodynamic variables are summarized in Figure 1-8.}
\]
1.2.2 Nonlinear Macroscopic Models

For most engineering applications, it is sufficient to apply linear theory to describe the piezoelectric effect. As the envelope of operation exceeds the small fields assumption, higher order theories are needed. Even for the traditional dielectric, at higher electric fields, electrostriction, which is fundamentally nonlinear, ceases to be negligible. As far as ferroelectrics are concerned, most of the important characteristics, such as hysteresis and polarization reversal, absolutely require nonlinear theories to describe them even in a qualitative sense. One way to extend the linear theory is to simply expand the thermodynamic potential to include an arbitrary number of higher order terms. However, such approach is often cumbersome and the number of additional higher order terms soon becomes prohibitive. In order to keep the theory economical, terms that are significant to certain nonlinearities are identified with the aid of physical insights. The following are some of the nonlinear models that have been developed.

1.2.3 Phenomenological Theory for Ferroelectrics [9]

Equilibrium states in crystals can be in general completely specified by three pairs of conjugate variables discussed in §1.2.1. By higher order expansion of thermodynamic potentials, some significant nonlinear phenomena can also be incorporated into the model. One of such theory was developed by Cady [34], and Devonshire [35] describes the
dielectric responses of ferroelectric crystals undergoing ferroelectric phase transition and polarization reversal. An extension to incorporate the elastic responses of ferroelectric crystals (ferroelasticity) was also developed.

The major assumptions of this theory are that both the electrical displacement and the electric field are aligned with one of the crystallographic axes. The nonpolar phase of the crystal is centrosymmetric and, all stresses are zero. With these assumptions, the elastic Gibbs energy $G_i$ can then be expanded into a Taylor series with temperature dependent coefficients of the form,

$$G_i = U - T_i S_{ij} - \sigma \Theta, \quad \frac{\beta(\Theta)}{2} D^2 + \frac{\gamma(\Theta)}{4} D^4 + \frac{\delta(\Theta)}{6} D^6. \quad (1.10)$$

The energy above is measured with respect to the nonpolar phase. However, both first and second order transitions can be demonstrated in a simple case with $\beta$ as the only temperature dependent coefficient. In addition, $\delta$ is required to be positive since the potential must be positive as $D$ approaches infinity. The order of the transition will be determined by the sign of $\gamma$; if it is positive, the transition will be second order, which the spontaneous polarization varies continuously across the Curie point. If $\gamma$ is negative, the transition will be first order, and the spontaneous polarization will be discontinuous at the Curie point.

The equation of states is obtained by differentiating (1.10) with respect to $D$. By using the knowledge that the dielectric permittivity approaches infinity at the Curie-Weiss temperatures ($\Theta_o$), the equation of states can be written as,

$$E = \beta_o (\Theta - \Theta_o) D + \gamma D^3 + \delta D^5. \quad (1.11)$$

Ferroelastic effects can also be described by this theory if the appropriate terms are augmented to the Gibbs energy [12]. However, the choice of higher order terms to retain in the expansion depends on the nature of the ferroelectricity in the material. For barium titanate, which is non-piezoelectric in the paraelectric phase, the following expansion can be used.

$$G_i = G^o(\Theta) - S^o(\Theta) T - \frac{s^o D^2}{2} + \frac{\beta^o T D^2}{2} + \frac{\gamma^o T D^4}{4} + \frac{\delta^o T D^6}{6} \quad \downarrow$$

$$S^o(\Theta) + s^o T - Q D^2$$

$$E = (\beta^o + 2Q T) D + \gamma^o T D^3 + \delta^o T D^5 \quad (1.12)$$

The electromechanical coupling that enters here is the electrostriction coefficient $Q$. There is also a normal thermal expansion term $S^o(\Theta)$ in the model. All the coefficients
with superscript $T$ are coefficients under constant stress. These equations in (1.12) are the nonlinear state equation of a barium titanate crystal. To illustrate that this model demonstrates piezoelectricity under small fields conditions, (1.12) can be linearized about $P_s$ to obtain the following approximation:

$$S - S^0 = s^0 T - (2QP_s)(D - P_s),$$
$$E = \beta^T D^2 + (2QP_s)T.$$  \hspace{1cm} (1.13)

Thus, the crystal displays linear piezoelectricity around $P_s$ when it is below the Curie point, and the piezoelectric coefficient that is induced by the spontaneous polarization is $2QP_s$.

The advantage of this model is that besides hysteresis and polarization reversal, it can capture a wide range of temperature effects, which are important in many applications. However, the theory can only be applied to crystals but not ceramics. This is because ceramics are polycrystalline solids which have no regular structure. Thus, the macroscopic states are not uniquely defined by the microscopic states, i.e., drastically different microscopic states of the crystallites can give the same macroscopic states in ceramic body. An infinite number of order parameters, such as polarization of the crystallites, will be needed to completely specify the equilibrium state of the material. This is a major disadvantage, since almost all the applications of ferroelectric materials involve ceramics. Another problem in restriction imposed by the model in practice is that only $D$ can be used as the independent variable. In many cases, electric field is the variable which is commanded. Since the model uses high order polynomials, it is very difficult to invert the state equations for field-commanded applications. A more serious limitation on the model is that the formulation is entirely based on the stress-free assumption. The stress state of the material has no effect on the state of the polarization. Thus, this model is unsuitable for modeling actuators, where the influence of stress on material state is obviously significant.

### 1.2.4 Internal Variables Model I

In modeling polarization reversal in ferroelectrics, it is important to recognize that the display of a hysteresis loop in the polarization–field relation and the butterfly loop in the strain–field relation, are due to domain growth, nucleation, and switching. Such processes are inherently time dependent and cannot be dealt with directly by simple phenomenological models such as the one in §1.2.3, in which time is not explicit in the formulation. Thus, Chen and co-workers formulated a class of semi-empirical phenomenological models based on a set of internal dynamic variables that represent the domain switching of ferroelectric ceramics. The model discussed in the following is based
on Reference 36. Other variants of the model and techniques in implementation are also discussed in References 37-42.

There are several assumptions for this model. First, the sample is a homogeneous continuous medium on the macroscopic scale. Second, the macroscopic electrical responses of the material can be represented by electric dipoles in the material whose components can be altered by external influences. Third, the sample is a plate type geometry and is under stress free, isothermal conditions. Fourth, there exists a virgin, or unpoled state of the material that has no net alignment of dipoles in any direction, and is completely isotropic. This state is referred to as the reference state.

Based on these assumptions, the constitutive relations can be represented in the general form of,

\[
\begin{align*}
\hat{T}(S,E,N) &= 0, \\
\hat{D}(S,E,N) &= 0, \\
\hat{N} - \hat{h}(E,N) &= 0.
\end{align*}
\]  

(1.14)

\(N\) is the non-dimensional internal variable that represents the effective number of dipoles aligned with the electric field, essentially the sum of projections of all the dipoles in the direction of the field. Its time history is governed by a nonlinear rate law which is only driven by the field. Together with Taylor expansions of the constitutive relations, (1.14) can be simplified to the form,

\[
\begin{align*}
T &= cS - eNE - a|N|, \\
D &= eNS + eE + bN, \\
\dot{N} + \alpha(E) &= \beta(E) = \alpha(E)N_e(E).
\end{align*}
\]  

(1.15)

The constants \(a, b, \) and \(e\) are all positive, describing the additional stress and electrical displacement due to domain switching and the piezoelectric effect generated by a nonvanishing net effective dipole. The rate function for switching, \(\alpha(E)\) has the following characteristics. 1) It must be a positive even function. 2) Increase monotonically with the magnitude of the field. 3) It must saturate at high enough field level. 4) It must vanish in the absence of an external field. \(N_e(E)\) is the total number of dipoles that can be switched at each field level. Thus, it is required that it has to be an odd function of field, increasing monotonically with the field and vanishing in the absence of an external field. In addition, it has to be bounded at all field levels. Typical shape of these two functions are shown in Figure 1-9. It has also been observed in real ferroelectrics that there are domains that are permanently switchable and also non-permanently switchable. To take into account such behavior, \(N\) is further split into two families that represent these two categories. Additional
inequality constraints are imposed on each of the family rate laws so that the permanently switchable dipoles will only switch if opposing field is applied.

![Graphs showing typical shapes of $\alpha(E)$ and $N_e(E)$](image)

Figure 1-9. Typical shapes of $\alpha(E)$ and $N_e(E)$ used in the rate law of Chen's model

This model can provide very accurate descriptions of the hysteresis loop and the butterfly loop for a constant field and frequency, when all the model parameters can be tightly tuned. The structure of the model is quite simple, which makes the simulations relatively straightforward. Introduction of the rate law also circumvents the difficulties in dealing with high order polynomials. However, the model parameters $\alpha(E)$ and $N_e(E)$ are obtained by manually fitting the model to experimental data. As a result, the resulting model is very sensitive to variations in magnitude and frequency of the input electric field. Furthermore, this is again a model formulated on the basis of stress-free conditions, which makes it unsuitable for actuation purposes. Extensions of the model with additional rate laws with strain as an input was also derived [38]. Difficulties in characterizing the model parameters prevented it from further studies.

### 1.2.7 Internal Variables Model II

From a more fundamental point of view, Chen's model can be classified as a model formulated in terms of the thermodynamics of irreversible processes. In parallel to the work of Lax and Nelson, Maugin and co-workers also developed a framework of a phenomenological model for deformable dielectrics based on irreversible thermodynamics [43-49]. The fundamentals of such a formulation are based not only on the first and second laws of thermodynamics, but also on the principle of virtual power for finite velocity fields. The characteristic of this type of model is that it involves a set of observable variables and a set of internal variables that govern the internal dissipation which gives rise to the hysteresis in the observable variables.
The model which this section sketches out is a variant of this type of theory based on the work of Bassiouny in References 50 and 51. The set of observable variables chosen consists of temperature, total strain, and instantaneous polarization. For a reversible process, the states of the material only depend on the values of these variables at any one time. With further simplifying assumptions, the only internal variable needed is for polarization. For irreversible processes, the state of the material depends not only on the observable variables, but also on the whole past history of the internal variable. It is important to note that this internal polarization represents the internal state of the material and cannot be controlled directly. A free energy function depending on both sets of variables is postulated and a set of constitutive relations are defined. By using the free energy function, the Clausius–Duhem inequality, and the second law of thermodynamics, the constitutive and the complementary constitutive equations can be derived. By further introducing the loading function and an electrical version of Drucker’s inequality, a theory that includes coupled electromechanical hysteresis can be derived. In Reference 51, the model was applied to describe the poling of ceramics, and the relation to Chen’s model was demonstrated.

While the framework of this model is very general due to its roots in rigorous irreversible thermodynamics, it is also extremely complex and difficult to implement. In essence, this model is directed towards the theoretical studies of thermodynamics of coupled systems rather than practical applications. Thus, this approach was not pursued in this study.

1.2.8 Miscellaneous

Apart from the above models, there are some other models developed recently that were used to account for some nonlinear behaviors of ferroelectrics. One model developed by Joshi [52] encompasses higher order effects such as electrostriction and elastostriction through higher order expansions of thermodynamic potentials. This approach to modeling in general is only adequate to indicate the kind of higher order effect that can be present along with linear piezoelectricity in ferroelectrics in a small field range. However, the severe lack of physical insight in such attempts often negates its usefulness in applications.

Another phenomenological model that was proposed by Zhang and Rogers [19] that uses the first and second law of thermodynamics and a continuum mechanics approach. This formulation targets the electromechanical coupling of ferroelectric ceramics under the stress-free, quasi-static influences of an external electric field. The polarization
reversal dynamics are not dealt with directly. The dielectric behavior of the ferroelectric, thus the shape of the hysteresis loop, is captured by a pair of hyperbolic tangent curves. By invoking the first and second law of thermodynamics, together with the Helmholtz free energy, a rate form of electromechanical constitutive relation can be derived. Material constants in the constitutive relation are defined by the derivatives of the Helmholtz free energy, which can only be determined by experiment. By using this constitutive relation and the proposed curve-fit to the hysteresis loop, the stress-free strain was then expressed in terms of external field alone.

Since the basic mechanism of polarization reversal was not dealt with in this model, it represents an ad hoc approach in capturing the nonlinear behaviors. The model is severely limited by the fit of the hysteresis loop in a constant field. Thus, the model is only applicable in stress-free condition with a single field level. It is of course possible to repair this deficiency by using a more realistic model of polarization instead of a curve fit. However, it is imperative for this model formulation to have an explicit functional form of such description of polarization. This can prove to be quite improbable due to the multi-value nature of the hysteresis loop. Because of these limits inherent to the model, it can only serve as another demonstration of the ability of irreversible thermodynamics in describing hysteretic systems.

1.3 APPROACH

It is fairly obvious from the previous discussions that none of the above models capture all of the important aspects of ferroelectric ceramics. Some of the models that were developed for ferroelectric crystals, such as Devonshire’s model, cannot be used at all to model most of the behaviors in ceramics. Further complications such as manufacturing process, grain size, and the addition of dopants also change ceramic properties. The fundamental issue that is not addressed in all these models is that the presence of crystallites in ceramics averages out many of the crystal properties due to their random orientations. To adequately model such phenomena, one would need to exploit the random nature of the ceramic structure by using a large number of internal degrees of freedom to represent the internal polarization of the crystallites. However, only very simple constitutive relations can be assumed for each crystallite in order to minimize the effort in computing the evolution of a large number of internal variables in such a model. Otherwise, the sheer amount of computational overhead is totally unrealistic in terms of engineering applications.
One of the most important issues is that all of the models discussed were
developed under a stress-free assumption. This assumption was often made in model
formulations in simplifying the derivation. In many cases, where the dielectric behavior is
of the main interest, models derived based on this assumption are often adequate.
However, when adapting them for modeling actuators, the results are far from satisfactory.
It was observed that in the presence of mechanical stress, the actual performance of the
ferroelectric actuator is far below the prediction given by the actuation strain assumption
even at fairly low field level. The source for the discrepancy is the dependence of the
actuation strain on the actual strain level of the ceramic [4, p.32]. Currently, there are no
well established methods available to correct resulted discrepancies.

The approach that will be used in the study is to model a ferroelectric ceramic with
a large number of families of internal variables that represents the electrical and mechanical
states of the crystallites. Thus, all the basic characteristics of the ferroelectric crystallites
such as piezoelectricity and polarization reversal can be captured in a microscopic level. The
macroscopic responses of the ceramic can then be calculated based on this collection of
microscopic crystallite states. Thus, the influence of applied stress on the material states can
be directly incorporated into the relations of the internal variables. Thus, a rather complete
model of a ferroelectric actuator including most of the relevant behavioral characteristics
can be achieved for quasi-static conditions.

The structure of this thesis is as follows. Chapter 2 will focus on the experimental
aspect of this project. Techniques for measuring some standard material properties will be
discussed. The experimental setups and procedures as well as necessary calculations to
obtain these material constants will be described in detail. The dependence of material
behaviors on electric field and strain will be characterized by a series of studies on the
extensional behavior of sandwich structures. This series of tests will provide all the
necessary insights to the important nonlinear effects during polarization reversal under
stresses. These general observations will guide the model development by dictating the
necessary features to be incorporated into the model.

Chapter 3 will contain the formulation of the phenomenological model with internal
variables for ferroelectric ceramics. The model is based on an idealized quasi-static model
of polarization reversal in a crystallite. The behavior of a general polycrystalline (ceramic)
system can then be extrapolated by considering a multitude of crystals rotated uniformly in
three dimensions. The resulting model is then specialized for piezoceramics with a thin
plate geometry for comparison with experimental results.

Chapter 4 will contain the model validation and discuss various issues involved in
the model simulations. Methods used to characterize various model parameters that are
unavailable for measurements will be discussed. Difficulties encountered during the simulations for the sandwich structures and techniques developed to overcome them will be elaborated. Finally, the model predictions will be compared to the experimental data from Chapter 2 to validate the model.

Chapter 5 will summarize and draw conclusions from the findings of this study. Further refinements of the model and future experiments will be proposed. Possible new applications of ferroelectrics resulting from the prediction capability of this model will also be suggested.
Chapter 2: Material Characterization

Before any rigorous modeling can be carried out for ferroelectric ceramics, their material behavior must be characterized. Thus, important effects observed during the characterization processes can be directly incorporated into the model development. The results of the characterization can also provide the necessary data to compare to the model predictions for validation purposes. The type of material behavior of interest in this study is the quasi-static linear and nonlinear dielectric and electromechanical behavior. Therefore, there are two parts to the characterization process. The first part is to measure some of the small field linear material properties of both poled and unpoled ceramics. This will provide an indication of the accuracy of the figures provided by the manufacturer, as well as a measure of consistency of quality in the batch of ceramics. All the measurements of the linear properties were done by the resonance frequency method recommended by the Institute of Radio Engineers Standards (IRE Standards). The second part is to characterize the high field nonlinear behavior of the material. Electric field applied to both free and partially clamped ceramics is slowly increased past the depoling field to induce polarization reversal. By monitoring the strain and the electrical displacement displayed in the material, the manner in which polarization reversal occurs in the ceramic under various loading conditions can be examined. The effects of large applied field and mechanical stress exerted by the clamping can be directly quantified. The result is also compared to the predictions by the actuation strain assumption to reveal the effect of induced stresses on the production of actuation strain in ferroelectrics.

2.1 CHARACTERIZATION OF LINEAR MATERIAL PROPERTIES BY THE RESONANCE FREQUENCY METHOD

Even though the material constants of the ceramics are not required at any stage of this study, they were measured to be compared with the manufacturer’s data sheet to verify the quality of the ceramic. Most of these material constants can be measured individually under quasi-static conditions. However, such an approach is often undesirable [53]. One of the most important reasons is that measurements from these quasi-static experiments often provide insufficient precision. In addition, to carry out a complete set of experiments to obtain elastic, piezoelectric, and dielectric properties is very laborious and time consuming. This approach also requires attaching strain gages and metal tabs for measuring stresses and strains, which means that these samples usually cannot be retrieved for use in other applications. More importantly, ceramics used for actuation are usually thin plate or disk
shapes and since ferroelectric ceramics are very fragile, it is extremely difficult to perform conventional experiments to measure data related to mechanical stiffnesses. An alternative procedure is to use the resonance frequency methods recommended in the IRE Standards [53-55]. This is a dynamic method which treats the sample as a vibrator and the resonance frequency of a vibrational mode is measured under the excitation of a small a.c. electric field. This method can circumvent all the difficulties present in the quasi-static method. Moreover, it can produce extremely accurate measurements, depending on the approximations used in the calculations. To characterize all the properties relevant to the planar geometry, only the capacitance, the magnitude of the minimum impedance, and the two resonance frequency measurements of a thin disk are required; the whole process can take less than fifteen minutes. Further measurements on the same sample with one split electrode can be carried out to obtain the Poisson’s ratio [56]. However, reasonably accurate measurements can be made by assuming a nominal Poisson’s ratio. Furthermore, there is no attachment of any kind on the sample used in this experiment; thus it can be retrieved and used for any other application.

The principle behind this method is a continuum model describing the vibrational motion of the sample and the linear piezoelectric constitutive relations. Piezoelectrics are particularly suited for this type of measurements because mechanical vibrations can be conveniently excited by an electrical input through piezoelectricity. In order to obtain a full set of material constants in three dimensions, samples of different geometry are needed. Thin circular disk, rectangular plates and cylindrical bars and cylinders are commonly used. This study, however, only involves properties that are in-plane with the sample and thus only the disk geometry is required to characterize the relevant constants.

2.1.1 Vibrator Model

Due to the existence of electromechanical coupling in piezoelectric, resonance of various mechanical vibration modes can be easily excited by applying a small a.c. voltage. The type of motion induced in the piezoelectric vibrator depends on the frequency of the applied field and the geometry of the material. For example, in a piezoelectric thin plate, both radial and longitudinal (through the plate thickness) vibrational modes can be induced. When the vibrator is very close to a resonance frequency, the vibrator can be modeled as a second order mechanical system coupled with a dielectric. It is also because of the electromechanical coupling that the mechanical properties of the vibrator can affect the electrical responses of the vibrator. Thus, the electrical behavior of a lightly damped
piezoelectric vibrator can be quite accurately represented by an equivalent circuit as shown in Figure 2-1 when close to mechanical resonance. The two terminals of the circuit correspond to the two electroded faces of the vibrator. One arm is made up of a serial rlc circuit, representing the mechanical admittance of the sample. Although the values of the circuit elements in the mechanical arm do not directly relate to the actual mechanical properties, their nature does correspond to various properties of a mechanical vibrator: the resistance $R_1$ represents damping, inductance $L_1$ represents inertia and capacitance $C_1$ represents elasticity. The shunting capacitance $C_0$ represents the dielectric part of the sample. Since the values of these parameters are associated with a specific vibrational mode, the values themselves are assumed to be frequency independent. This assumption is only valid when the mode in consideration is sufficiently isolated from the other modes [54]. Therefore, the first vibrational mode is usually considered because it has the largest frequency separation from the other modes. In addition, ferroelectric ceramics generally have high density and Young's modulus, resulting in a very high resonance frequency. Measuring the resonance frequencies of any mode beyond the first one presents numerous instrumentation difficulties. In the case of a circular disk, the first extensional mode is a radial mode with a node at the center of the disk.

![Equivalent circuit](image)

Figure 2-1. An equivalent circuit for a piezoelectric ceramic near resonance.

The impedance of the equivalent circuit, $Z$, can be written as,

$$Z = \frac{1}{2\pi f C_0} \frac{\Omega - j\delta}{1 - \Omega + j\delta}, \quad (2.1)$$

where $\Omega = \frac{f^2 - f_s^2}{f_p^2 - f_s^2}$ and $\delta = 2\pi f C_0 R_1$. All of the above frequencies are in Hertz. The two characteristic frequencies $f_s$ and $f_p$ are the motional (series) resonance frequency and the parallel (lossless) resonance frequency, respectively. They are given by,

---

1 In the case when the sample is not completely flat, an out of plane bending mode can be excited. However, this is not the vibrational mode that was considered in the resonance frequency method, and one can notice that in the experiment by realizing that the observed resonance frequency of a bending mode is much lower than that of an extensional mode. Therefore when the ceramic was driven at the resonance frequency of the radial extensional mode, the contribution from bending should be negligible.
\[ f_s = \frac{1}{2\pi\sqrt{L_1C_1}}, \quad f_p = \frac{1}{2\pi\sqrt{\frac{L_1}{C_1+C_{1'}}}} \]  

(2.2)

The significance of \( f_s \) is that the reactance of the \( rlc \) branch, \( X_1 \), vanishes at this frequency. Similarly, \( f_p \) is the frequency at which the resistive component of the overall network impedance, \( R_e \) (the real part of \( Z \)), is at a maximum. Another two characteristic frequencies can be defined by considering the reactance part of the network, \( X_e \) (the imaginary part of \( Z \)). The two frequencies at which \( X_e \) vanishes are defined as the resonance frequency \( f_r \), the antiresonance frequency \( f_a \). Finally, there are also frequencies at which the magnitude of the sample impedance \( |Z| \) is at a minimum and maximum impedance, \( f_m \) and \( f_n \). For a first approximation, \( f_s \) and \( f_p \) can be assumed to be equal to \( f_m \) and \( f_n \), respectively (Figure 2-2). The differences of the pairs of frequencies are as follows,

\[ (f_a - f_m) > (f_p - f_s) > (f_a - f_r). \]  

(2.3)

In samples with high coupling, mechanical, and dielectric quality factors, these differences are nearly equal. Provided that all the values for all four elements in the equivalent circuit are measured, there are equations in Table 2 of Reference 57 which solutions give the values of all six characteristic frequencies. However, such complete measurements are not needed in many instances, and some approximations can be used instead. A summary of these approximations and their associated errors can be found in Table 4 and 5 of Reference 57. If these approximations are used, only a portion of the measurements of values of the circuit elements are required. These simplifications usually do not introduce any significant error.

Depending on the type of the sample, different pairs of frequencies become important. If the loss in the sample is small, simple approximation for \( f_s \) and \( f_p \) using \( f_m \) and \( f_n \) will suffice. However, when loss is high, better approximations for \( f_s \) and \( f_p \) have to be used. In any case, the equivalent circuit parameters are determined to obtain all relevant quantities in the calculations of the desired frequency difference. However, in the context of this study, the goal is to obtain only a number of the planar material properties of a ceramic specimen, thus none of the parameters are needed directly. This greatly simplified the experiments and the calculations.
2.1.2 Resonance Circuit and Testing Procedure

The method to measure resonance frequency is to put the sample in a transmission network and observe the output of the circuit. The circuit is designed in such a way that the maximum and minimum output frequencies of the circuit are the minimum and maximum impedance frequencies of the sample. There are a few choices in selecting a circuit to measure all the vibrator model parameters. Frequency scan analyzers can also be used, though the sampling rates of most digital analyzers are well below the required rate for the target frequency range. The circuit that is recommended in all of the IRE Standards [53-55] is the Π-type transmission circuit, which was used in this study. The schematic of the circuit used is shown in Figure 2-3. The name of the network originated from the shape of the circuit; the sample is sitting in the middle of the circuit, with symmetrical input and output arms.
Figure 2-3. Schematic drawing of the Π-type transmission circuit used to measure material constants of piezoelectric wafers.

**Circuit Requirements**

Since the circuit is required to run at high frequency, many precautions must be taken in the design as well as in using the circuit. A signal generator with high frequency stability and waveform purity is used to provide the a.c. voltage to the network. The terminating resistor $R_T$ should be at least smaller than $H$ of the minimum impedance of the sample; the smaller the resistance of $R_T$, the sharper the observed resonance peak is. The resistor $R_i$ is the isolating resistor, which should be at least $10R_T$ so that the external characteristics of the signal generator and the detector impedance can be neglected [58]. Since the transmission circuit has low input impedance compared to the signal generator, a large isolating resistance can also be used to increase the input impedance of the network to prevent a significant drop of voltage at the output of the signal generator. In addition, the frequency of the input sinusoid is measured by a high accuracy frequency counter. The output of the network is then observed on a standard analog oscilloscope.

In constructing the transmission network, great attention must be paid to the layout of the circuit. Since the network operates at high frequency, the entire circuit must be electrically shielded from the external environment to prevent noise from polluting the signal in the circuit. In addition, the input, output arm, and the sample must also be shielded from each other in separate compartments, as indicated in Figure 2-3, to eliminate crosstalk between different parts of the circuit. If the test sample has low dielectric constants, additional care should be taken to minimize the stray capacitance between each terminal of the sample and ground. For samples with small diameter to thickness ratio, it should be adequately shielded on the side to minimize fringing capacitance [53]. Measurement errors inherent to the circuit can be further minimized or eliminated by
adding a shunting variable inductor across the sample, so that it can be tuned to resonate with the shunting capacitance $C_0$ in the equivalent circuit at $f_x$. All external connections from the instruments to the circuit should be made by coaxial cables to prevent picking up noise due to interference.

During the nominal operation of the network, the switch is at position B, where the sample is directly connected to the input and output arms of the circuit. This is known as the series resonance operation mode [54]. In this mode, the frequencies of the maximum and minimum transmission, $f_m$ and $f_n$, are measured by varying the frequency of the input sinusoid. The amplitude of the output voltage at the maximum transmission frequency is also recorded. To measure the magnitude of the minimum impedance of the sample, the switch is set to position A and the input frequency set to $f_m$. The variable resistor will then be adjusted to a value so that the output level of the circuit is the same as the recorded value at $f_m$ with the sample in place. If the motional capacitance $C_1$ in the equivalent circuit is needed, the switch is then set to C or D. Then the network is in the positive reactance operation mode [54]. The frequency at maximum transmission is measured again with each of the two different capacitors in series with the sample. Using the three maximum transmission frequencies and the two capacitances, $C_1$ can be determined [54].

**Implementation of Transmission Circuit**

In the transmission circuit used, the signal was generated by a Philips PM 5138 function generator with an output impedance of 50 $\Omega$. The frequency of the input sinusoid was measured by a Philips PM 6669 universal frequency counter (120 MHz). The output of the circuit was observed on an Tektronics 2235 100 MHz analog oscilloscope. $R_n$ is a single turn 10 $\Omega$ variable resistor. The values of all other circuit elements are as indicated in Figure 2-3. In determining the minimum transmission frequency, $f_n$, a 10.2 $\Omega$ resistor was used instead of 1.1 $\Omega$ resistor $R_T$ to increase the sensitivity of the circuit [53]. A shunting inductor was not used in this experiment because none of the circuit parameters required direct measurements. Since the sample was ceramic, the high internal mechanical dissipation allowed a rather crude sample holder to be used, as shown in Figure 2-4. The holder was constructed in such a way that the connection to the electrodes of the sample runs in a straight line, to minimize crosstalk between the input and the output. A pair of aluminum pointed contacts are used to hold the sample at the center. Thus, the contacts will be made at the node of the vibrational mode and the mode shape would not be altered by the sample holder. The main body of the sample holder were constructed from a single
piece of plexi-glass. Each of the springs are made of a single sheet of 25 mil stainless steel plates.

![Diagram of sample holder for resonant testing.]

**Figure 2-4. Sample holder for resonant testing.**

**Experimental Procedure**

The ceramic used in the experiments are PZT–5H manufactured by Morgan Matroc, Inc. The dimensions of the supplied wafers are 2 inch by 1 inch by 12.5 mil thick. The wafer also has nickel electrodes electroplated on both faces and proper poling and aging procedures were carried out by the manufacturer. This ensures that the maximum amount of remanent polarization is achieved in the ceramics. Five samples were picked out at random for the resonance tests. They were first cut into square plates of 1 inch by 1 inch and then machined into circular disks of 1 inch diameter. Both the radius and the thickness of the disks were measured and the electrodes of an extra sample were completely etched off using ferric chloride solution to verify the thickness of the metal electrodes. The result indicated that the electrode thickness is negligible.

The constants that are of interest are \( s_{11}^E \), the in-plane compliance under constant electric field, \( \varepsilon_{33}^t \), the dielectric constant in the poling direction and \( d_{31} \), the piezoelectric strain constant. To obtain all these quantities, four different measurements are required; the low frequency capacitance, frequency at maximum and minimum transmission, and the magnitude of the impedance at minimum transmission. From these measurements, all of the above properties can be determined from the procedure from Reference 53. The analysis will be carried out in §2.1.3.

First, the dimensions of all the samples were measured. Then, the low frequency capacitance of the sample was measured by a Leader LCR-740 bridge operating at 1 kHz. Five independent capacitance measurements were made for each sample. This capacitance is equal to \( C_0 + C_1 \), and is used to determine the dielectric permittivity of the material.
Second, the samples were put into the sample holder to measure $f_m$ and $f_n$. The frequency of the applied 1 V sinusoidal voltage was slowly raised from low frequency until the amplitude of the output observed was maximum (impedance was minimum). Both the frequency and the amplitude of the output were noted, as they would be needed in the measurement of the minimum impedance, $|Z_m|$. In the measurement of $f_n$, the sensing resistor $R_T$ was first changed into a 10.2 Ω resistor to increase the sensitivity. $f_n$ was found by adjusting the frequency of the input voltage until the output of the network was at a minimum (impedance was maximum). Finally, the sensing resistor $R_T$ was reset back to 1.1 Ω, and $|Z_m|$ was measured by using the variable resistor $R_{st}$. The frequency of the applied voltage was first set to $f_m$, the variable resistor was then adjusted to a value so that the network output is the same level as when the sample was in place. This value of the resistor was used as $|Z_m|$.

**Measurements on Unpoled PZT**

In addition to the small field material properties of the poled ceramics, the compliance and the dielectric permittivity of unpoled ceramics were also measured. Since the unpoled ceramics are mechanically and electrically isotropic, there are only two required measurements, $s_{11}$ and $\varepsilon_{33}$.

Since all the PZT–5H wafers were poled in the factory, unpoled ceramics were obtained by thermally depoling the poled wafers. Two of the disks used in the first series of characterizations was submerged in the Neslab EX–250 silicon oil bath. Then the temperature was raised from room temperature to 250°C. After holding at 250°C for 15 minutes, the heating element was switched off. The disks were left to slowly cool back to room temperature in the bath to avoid any thermal shock on the ceramics. Since the Curie point of PZT–5H is at 205°C, all the remanent polarization in the ceramics should be lost when put through such process. Afterwards, the disks were cleaned thoroughly by degreaser.

Between the two quantities, the simpler measurement is $\varepsilon_{33}$; the capacitance of an unpoled sample is simply measured again in the LCR bridge and the same calculations are followed. The measurement of $s_{11}$ is not quite as straightforward. Since unpoled PZT has no piezoelectricity, the mechanical resonance cannot be easily excited as in poled PZT. Thus the aforementioned procedure cannot be used directly and a modified approach was required. The two depoled samples were first mounted on top of two other poled samples from the previous test. Miller–Stephenson Epoxy 907 was used for the mounting with a small dot of conducting epoxy placed in the middle of the interface. The two sides of the
unpoled samples were then shorted using silver paint on the edges to provide electrical contact to the active piece at the interface. The composites were then compressed under 25 lbs of weight overnight to complete the cure cycle. The maximum transmission frequency of the composites was then measured to find the combined compliance of the composites.

2.1.3 Results and Analysis

After the four measurements described in §2.1 were carried out, the equations in Reference 53 can be used to calculate all the required material constants. First, the figure of merit of the sample is calculated by the approximation,

\[ M = \frac{1}{2 \pi f_s R \omega C_o} = \frac{1}{2 \pi f_m |Z_m|(C_o + C_1)}, \]

(2.4)

where \( |Z_m| \) is the magnitude of the minimum impedance and the unit of \( f_m \) is in Hertz. Then the frequency difference \( f_p - f_s \) is approximated by,

\[ \Delta f = (f_p - f_s) = \frac{(f_p - f_m)}{\sqrt{1 + \frac{4}{M^2}}}. \]

(2.5)

All the material constants can then be calculated with the following equations. The resulting average figure of merit from (2.4) is 17.23. Thus the result of (2.5) is that the two pairs of frequency differences are within 1% of each other. Together with the relation given by (2.3), \( f_m \) was determined to be an adequate approximation of \( f_s \), and therefore \( f_s = f_m \) was used in all of the following calculations. The planar coupling factor \( k_p \) is then given by the following equation for a circular disk.

\[ k_p^2 = \frac{(1 - \nu^E) J_1[\eta(1 + \Delta f/f_s)] - \eta(1 + \Delta f/f_s) J_0[\eta(1 + \Delta f/f_s)]}{2 J_1[\eta(1 + \Delta f/f_s)] - \eta(1 + \Delta f/f_s) J_0[\eta(1 + \Delta f/f_s)]}, \]

(2.6)

where \( J_o \) and \( J_1 \) are Bessel functions of the first kind and zero and first order, respectively. \( \eta \) is the lowest positive root of the equation \( (1 - \nu^E) J_1(\eta) = \eta J_0(\eta) \). \( \nu^E \) is the Poisson’s ratio between the two planar axes. The typical value for PZT is between 0.29 to 0.33. However, the solution of (2.6) is rather insensitive to the exact value of \( \nu^E \) in the given range [53], and a nominal value of 0.31 was thus assumed in all the calculations, as suggested by the manufacturer. The effect of this uncertainty was accounted for in the

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2 The corresponding equation in Reference 53 contains a sign error.
actual error analysis of the data. The rest of the properties were calculated with the following equations.

\[ k_{31} = k_p \sqrt{\frac{1 - \nu^E}{2}}, \]

\[ \varepsilon^T_{33} = \frac{4t(C_o + C_1)}{\pi d}, \]

\[ s_{11}^E = \frac{\eta_1^2}{\pi^2 d^2 f_s^2 (1 - (\nu^E)^2)} \rho, \]

\[ d_{31} = k_{31} \sqrt{\varepsilon^T_{33} s_{11}^E}, \tag{2.7} \]

where \( t \) and \( d \) are the thickness and the diameter of the disk, respectively. \( \rho \) is the density of ceramic, which was not measured directly. This is because the small size and weight of the samples impose severe restrictions on the achievable accuracy. Thus, the manufacturer's figure of 7500 kg/m\(^3\) was used instead. As for the stiffness of the unpoled ceramics, \( f_m \) of the composites as used in (2.7) to find the combined compliance of the composites. The new compliance is the average between the poled disk and the unpoled disk. Since the compliance of the active disks are now known, the compliances of the unpoled disks can be calculated using

\[ s_{11}^{unpoled} = 2s_{11}^{comp} - s_{11}^E. \tag{2.8} \]

An uncertainty analysis was performed on this set of measurements. The mean and standard deviation of each measurement were calculated from the results of (2.4) to (2.8) from all five samples. The total uncertainty of each measurement was obtained by combining the measurement error from experiments and the statistical variation of the measurement from the five samples. Finally, the percentage error was calculated using the mean and the total uncertainty of each measurement. This is an estimate of the error associated with the measurement, not the deviation from the manufacturer's figures. A summary of the results is provided in the following table. All the results of the analysis and a complete uncertainty analysis are summarized in Appendix A.
Table 2-1 Result of Resonance Frequency Test. (N/A denotes figures that are not available.)

<table>
<thead>
<tr>
<th>Manufacturer's Figure</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Total Uncertainty</th>
<th>Percentage Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{33}$ ($F/m^2$)</td>
<td>3.006x10^{-8}</td>
<td>2.945x10^{-8}</td>
<td>1.267x10^{-9}</td>
<td>4.302</td>
</tr>
<tr>
<td>$\varepsilon$ ($F/m^2$)</td>
<td>N/A</td>
<td>1.914x10^{-8}</td>
<td>8.275x10^{-10}</td>
<td>4.323</td>
</tr>
<tr>
<td>$k_p$</td>
<td>0.650</td>
<td>0.626</td>
<td>0.019</td>
<td>3.997</td>
</tr>
<tr>
<td>$k_{31}$</td>
<td>0.390</td>
<td>0.368</td>
<td>0.011</td>
<td>4.938</td>
</tr>
<tr>
<td>$s_{11}^E$ ($m^2/N$)</td>
<td>1.65x10^{-11}</td>
<td>1.559x10^{-11}</td>
<td>1.049x10^{-12}</td>
<td>6.730</td>
</tr>
<tr>
<td>$s_{11}$ ($m^2/N$)</td>
<td>N/A</td>
<td>1.383x10^{-11}</td>
<td>N/A3</td>
<td>6.730</td>
</tr>
<tr>
<td>$d_{31}$ ($m/V$)</td>
<td>2.74x10^{-10}</td>
<td>2.491x10^{-10}</td>
<td>1.738x10^{-11}</td>
<td>6.974</td>
</tr>
<tr>
<td>$M$</td>
<td>N/A</td>
<td>17.228</td>
<td>1.216</td>
<td>9.844</td>
</tr>
</tbody>
</table>

The uncertainties shown above include least count errors of the instruments, the uncertainty in $\nu^E$, as well as the statistical uncertainties at a 95% confidence level due to the small sample number of the test. The result of this test resulted in very good agreement with the standard properties of PZT-5H as provided by the manufacturer; all the quantities except $d_{31}$ fall in the full range of the measured result. It is important to point out that the larger uncertainties in $s_{11}^E$ and $d_{31}$ is the direct result of the large uncertainty in $\nu^E$ (2.7). If $\nu^E$ were measured directly, the resulting uncertainties would be about an order of magnitude less than present values, indicating the tremendous accuracy of the resonance frequency technique.

2.2 NONLINEAR PROPERTIES: EXPERIMENTS ON SANDWICH STRUCTURES

To characterize the behavior of PZT-5H during polarization reversal under applied stresses, a series of experiments were carried out on a group of sandwich structures. The reason for choosing this configuration is because of the simplicity of the structure. Each sandwich is made up of a square PZT wafer sandwiched by two pieces of metal of same lateral dimensions. By varying the thickness of the metal pieces, varying degrees of mechanical constraint can be achieved. The mechanical loading from the host structure in this case is in the plane of the actuator, perpendicular to the poling direction. The strain and

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3 Since there are only single measurements of compliances for each of the two samples, the standard deviation is not calculated.
electrical displacement of the sandwich were measured while a low frequency a.c. voltage was applied to the sandwich.

2.2.1 Preparation of Test Structures

The sandwiches were constructed of a 1 inch by 1 inch PZT–5H wafer in between two pieces of metal with equal thickness. Five groups of five sandwiches were manufactured. The metals chosen were 1.5 mil and 2.5 mil brass shim stock, and 20 mil, 40 mil and 60 mil aluminum 2024 plates. Finally, there is a group of five free wafers. A summary of the physical properties of the sandwich structures are presented in the following table.

Table 2-2. Summary of physical properties of sandwich structures. The relative stiffness $\psi$ is defined as $\psi = \frac{2c_s A_t}{c_p A_p}$, where $A$ is the cross sectional area.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_s$ (GPa)</th>
<th>$\nu_s$</th>
<th>$c_s$ (GPa)</th>
<th>$\psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>free</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1.5 mil brass</td>
<td>105</td>
<td>0.33</td>
<td>117.83</td>
<td>0.46</td>
</tr>
<tr>
<td>2 mil brass</td>
<td>105</td>
<td>0.33</td>
<td>117.83</td>
<td>0.61</td>
</tr>
<tr>
<td>20 mil Aluminum</td>
<td>70</td>
<td>0.33</td>
<td>78.55</td>
<td>4.05</td>
</tr>
<tr>
<td>40 mil Aluminum</td>
<td>70</td>
<td>0.33</td>
<td>78.55</td>
<td>8.11</td>
</tr>
<tr>
<td>60 mil Aluminum</td>
<td>70</td>
<td>0.33</td>
<td>78.55</td>
<td>12.16</td>
</tr>
</tbody>
</table>

$c_p = 62$ GPa, $t_p = 12.5$ mil.

Each type of metal was cut into 1 inch squares. The PZT wafers were then cut to the desired dimensions from the original size. The edges of the wafers were then slightly sanded to ensure that the electrodes were not shorted. The wafers were then cleaned after the dimensions were measured. There are three steps in the cleaning process; the electrodes on both sides were first cleaned with methanol to remove any grease. A mild acid was then applied to the electrode to remove oxides on the electrodes. Finally, a mild base solution was applied to neutralize the excess acid. The metal squares were first measured and sanded slightly, then cleaned with methanol to remove any dust, remove oxides, and roughen the surface to provide an effective bonding surface. After that, they were subjected to the same cleaning process as the ceramic. The metal squares were then bonded to the PZT using Hysol Epoxy Patch and were cured under 25 lbs of weight over night at room temperature. Electrical contact between the electrodes on the wafer and the metal on both sides was made by putting a small amount of conducting epoxy at the center of each
bonding surface. Finally, a strain gage was mounted on top of each sandwich using M-Bond 200 adhesive from the Measurement Group. The thickness of the finished sandwiches was then measured to determine the thickness of the bonding layers. The results of the measurements are summarized in Table 2-3. It is interesting to note that as the thickness of the metal squares decreases, the bonding layer thickness increases. This primarily due the difficulties encountered in flattening the shim stocks used. As a result, it was difficult to obtain a uniformly thin bonding layer in the sandwich. Another problem is that shim stocks tend to be much smoother than aluminum plates used. Thus, the epoxy tend to be less effective in bonding to the ceramic, and a thickness layer was required to guarantee successful assembly.

Table 2-3. Summary of measurements of bonding layer thicknesses of sandwich structures. All figures represents the thickness of one single bonding layer measured in mil.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 mil brass</td>
<td>1.0</td>
<td>1.0</td>
<td>0.75</td>
<td>1.25</td>
<td>1.0</td>
</tr>
<tr>
<td>2 mil brass</td>
<td>0.7</td>
<td>0.7</td>
<td>0.45</td>
<td>0.7</td>
<td>0.95</td>
</tr>
<tr>
<td>20 mil Aluminum</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>40 mil Aluminum</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>60 mil Aluminum</td>
<td>0.2</td>
<td>0.7</td>
<td>0.2</td>
<td>0.45</td>
<td>0.45</td>
</tr>
</tbody>
</table>

2.2.2 Experimental Setup and Procedures

Three variables were observed in this series of experiments: voltage applied to the sandwiches, the electrical displacement (charge) on the PZT, and the strain induced on the structures. The schematic of the circuit used for the measurements is illustrated in Figure 2-5. The primary loop in the circuit is the high voltage loop. The voltage driving the structure was supplied by a Kepco BOP 1000M bipolar amplifier with a gain of 100. The amplifier was operating in the voltage amplifier mode with a peak output of ±1000 V and a current limit of ±40 mA. The a.c. signal was supplied to the amplifier by a Phillips 5191 function generator. A 100 Ω resistor ($R_s$) was placed in series with the sandwich to allow for current measurements. The voltage applied to the sandwich was directly measured by a differential amplifier with gain of 0.01. Since the differential amplifier used is an inverting type, the voltage reading was then fed into an inverter to restore the sign of the signal.
$R_s=100\ \Omega$

$R_1=10\ \text{M}\Omega$, $R_2=100\ \text{K}\Omega,$

$R_3=100\ \text{K}\Omega$, $R_5=21.2\ \text{K}\Omega,$

$R_6=20\ \text{M}\Omega$, $C_6=4.7\ \mu\text{F}$

Figure 2-5. Schematic drawing of the charge and voltage measurement circuit.

The electrical displacement on the PZT was observed by integrating the current signal provided by the sensing resistor ($R_s$). The voltage across the resistor was fed through an integrator circuit. The capacitor in the integrator was shunted by a resistor to prevent the integrator from being saturated. The resulting time constant was set to be 94.5 seconds, so that it would not affect the overall operation of the integrator around the desired frequency of 0.3 Hz. The crossover frequency of the circuit was tuned to be 1 rad/s to approximate a unit integrator. Since this circuit is also inverting in nature, the charge signal was also fed into an inverter to restore the sign. An alternative to this circuit is the commonly used modified Sawyer–Tower circuit as shown in Figure 2-6 [59]. The modified Sawyer–Tower circuit has the advantage of being able to compensate for the conductivity of a sample that is linear to the applied voltage by tuning a variable resistor and capacitor. Since ferroelectrics in general, both crystals and ceramics, are not perfect insulators, the small current that is conducted will result in a more rounded hysteresis loop. The disadvantage of such a circuit is that there is no reliable way to calibrate the output charge signal accurately to a certain unit due to the varying capacitance of the sample. In contrast, the current integrating circuit can be easily calibrated by applying sinusoidal voltages of known frequencies. However, there is no way to compensate for the conducting effect in the current scheme. Under the conditions of this experiment, the conductivity of the PZT ceramics is rather low and thus the integrator approach was chosen.
The strain signal from the strain gage is measured by a Vishay 2120A strain gages conditioner powered by a Vishay 2110 power supply from Measurements Group. All the strain gages were mounted on the ground side of the sample to prevent noise due to interference from entering the strain signal. A half bridge configuration was used with the conditioner, with the test sample in the active arm of the bridge and another similar sandwich in the opposite arm to serve as a dummy gage to compensate for temperature variation. Finally, all three channels of data were collected and sampled at 75 Hz by a LabView system from National Instruments on a Macintosh Quadra 950.

An 0.3 Hz a.c. voltage was applied to the test samples. The voltage was slowly raised to six predetermined peak-to-peak levels to cover the whole process of polarization reversal. One whole cycle of data was taken at each level after steady state was reached. After the final cycle of data was taken, the voltage was reduced slowly to avoid any large current in the circuit. Generally, there are some variations in the PZT wafers in terms of material behavior, and also variations of bonding layer thicknesses and other factors related to the manufacturing of the specimens. Therefore, the strain and electrical displacement time signal from the five samples in the same group were then averaged together pointwise in time to obtain a nominal behavior, thus smooth out the effects of variations, and also reducing the effect of noise in the measurements. A summary of all the tests are presented in the following table.

Table 2-4. Summary of tests carried out on the sandwich structures

<table>
<thead>
<tr>
<th>Number of sample in each group</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range of relative stiffness (ψ)</td>
<td>0.00, 0.46, 0.61, 4.05, 8.11, 12.16</td>
</tr>
<tr>
<td>Peak field levels (V/mm)</td>
<td>472.4, 629.9, 708.7, 787.4, 866.1, 944.9</td>
</tr>
</tbody>
</table>
2.2.3 Experimental Results

Although the manufacturing process was quite successful in producing sandwiches with the thicker aluminum plates, producing sandwiches with the thinner shim stocks presented certain complications. Since the shim stocks are stored as rolls, they possess an inherent curvature which made it difficult to obtain a uniform bonding layer even when the sandwiches were cured in compression. The stainless steel shim stock proved to be too stiff to be flattened without significantly deforming the squares. For the thinner brass shim, the material was so compliant that wrinkles were easily impressed on the shim during the bonding process. Thus sandwiches made with these thinner materials tended to have thicker bonding layers. Measurements of the thicknesses of the finished specimens indicated that the thickness of the bonding layers for aluminum sandwiches was about 0.2 mil, which is smaller than the resolution of the micrometer used. However, for sandwiches made with shim stocks, the bonding layer thicknesses range from 0.5 mil to 1.25 mil thick.

The general performance of the five sandwiches in the same group remained quite uniform; the field level at which polarization reversal of the bulk material occurred and the amount of remanent polarization remained quite consistent over all the samples. The amount of peak to peak strain induced in the structure of the same thickness was also quite consistent, though there were some visible variations from sample to sample. The typical behavior of the ceramic at high fields is best illustrated by the data obtained from the unrestrained samples, as shown in Figure 2-7.
Figure 2-7(a-c). The progression of polarization reversal in a stress-free PZT wafer under increasing applied field. The peak applied field is 0.3 Hz, with amplitude (a) 472.4 V/mm, (b) 629.9 V/mm, (c) 708.7 V/mm.
Figure 2-7(d-f). The progression of polarization reversal in a stress-free PZT wafer under increasing applied field. The peak applied field is 0.3 Hz, with amplitude (d) 787.4 V/mm, (e) 866.1 V/mm, and (f) 944.9 V/mm.

The first field level at which data were taken was already beyond the small field region, as indicated by the amount of hysteresis observed (Figure 2-7a). As the field level was further increased, the slope of the strain–field hysteresis loop (the S–E loop) began to decrease while the amount of hysteresis increased dramatically (Figure 2-7b). When the applied field reaches a critical level, a small amount of polarization started to reverse direction, as indicated by the emergence of a small second loop on the right hand side of
the S–E loop (Figure 2-7c). Notice that the height of the electrical displacement–field hysteresis loop (the D–E loop) also increases significantly at this field level. Since most of the domains remained locked in their initial position, a saturation in the lower left hand corner of the D–E loop could also be observed, whereas the opposite corner remained rounded. As the field level was further increased, both the S–E loop and the D–E loop approached saturation on both sides, and a full polarization reversal was achieved in every cycle of the applied field (Figure 2-7d, e, f).

2.2.4 Actuation Strain Assumption

In predicting the overall strain induced in a structure by a solid state actuator, the conventional approach is to use the actuation strain assumption. The strain of the actuator is then modeled as,

\[ S_{total} = S_{mechanical} + \Lambda, \]  

(2.9)

where \( \Lambda \) is known as the actuation strain produced by the actuator. In ferroelectric actuators, that will be the strain produced by the electromechanical coupling. In the unrestrained situation there will be no mechanical strain present, and thus the actuation strain is equal to the free strain of the ceramic. When the ceramic is attached to a structure, (2.9) is then coupled into the computation of the structural strain. This model neglects all the details of the sources of the actuation strain and assumes that the presence of stress in the actuator does not change the properties of the actuator or the actuation strain produced. While this assumption is valid for some materials, such as electrostrictives [60], it is not necessarily correct for ferroelectrics. As in the discussions in the previous chapter, the electromechanical coupling is also affected by the stresses in the material. To determine the applicability of the actuation strain assumption to ferroelectrics, the induced strain on the sandwich structure was calculated using the strain data from the unrestrained samples with this assumption and was compared to the experimental results. Since the bonding layers were quite thick in some cases (comparable to the structural thickness), the most general case of two-dimensional extension that includes first order shear lag effects of the epoxy will give a solution that describes the effect of the bonding layer. However, the equations involved in the two-dimensional case are extremely complicated. Analytical solution of the two-dimensional case does not appear to be possible. Therefore, only the one-dimensional case was considered, which is based on the development of Reference 61.
Figure 2-8. Free body diagram of the cross section of a sandwich structure

Consider the configuration in Figure 2-8, with the PZT embedded between two layers of metal. Connecting them are two layers of epoxy that are allowed to shear along the surface of the plate. Material shear in the metal and PZT is neglected. The free body diagram of the typical cross section was only illustrates a one dimensional structure. However, due to the symmetry in the structure, the equilibrium condition along the y-direction is similar. By applying equilibrium conditions in both directions, the following relations can be derived:

$$\frac{dT_p}{dx} - \frac{\tau}{t_s} = 0, \quad \frac{dT_p}{dx} + \frac{2\tau}{t_p} = 0,$$

with

$$T_s = c_s S_s = c_s \frac{\partial u_s}{\partial x},$$

$$T_p = c_p^E (S_p - \Lambda) = c_p^E (\frac{\partial u_p}{\partial x} - \Lambda),$$

$$\tau = G\gamma = \frac{G}{t_b} (u_s - u_p),$$

where $c_s$, $c_p^E$, and $G$ are the stiffnesses of the structure and the PZT, and the shear modulus of the epoxy. After substituting (2.11) into (2.10), the governing differential equations become,

$$c_s \frac{\partial^2 S_s}{\partial x^2} - \frac{G}{t_s t_b} (S_s - S_p) = 0,$$

$$c_p^E \frac{\partial^2 S_p}{\partial x^2} + \frac{2G}{t_p t_b} (S_s - S_p) = 0.$$
These two coupled, second order differential equations do not depend on the actuation strain. This is because $\Lambda$ is assumed to be independent of the position. They can be further decoupled and solved independently by differentiating twice to obtain,

$$\frac{d^4 S^t}{dx^4} - \Gamma^2 \frac{d^2 S^t}{dx^2} = 0, \quad \frac{d^4 S^p}{dx^4} - \Gamma^2 \frac{d^2 S^p}{dx^2} = 0$$

(2.13)

where $\Gamma^2 = \frac{G(\psi + 1)}{c_{sl}t_b}$, called the shear lag parameter, approaches infinity when the bonding layer is infinitely thin, or infinitely stiff. $\psi = \frac{2c_{sl}t_b}{c_E t_{lep}}$ is the relative stiffness of the structure, which is the ratio between the extensional stiffness of the metal and the PZT. Since (2.13) originated from two second order equations, their solutions are coupled and have four degrees of freedom in determining the solutions. Furthermore, since the structure is symmetric along the $x$-axis, only two boundary conditions are needed to determine the coefficients in the solution. By choosing $S_p(l) = \Lambda$ and $S_s(l) = 0$ as the boundary conditions, the following solutions are obtained:

$$\begin{bmatrix} S_p \\ S_s \end{bmatrix} = \begin{bmatrix} \Lambda \\ 1 + \psi \end{bmatrix} \begin{bmatrix} 1 + \psi & \frac{\cosh \Gamma x}{\cosh \Gamma l} \\ \frac{\cosh \Gamma x}{\cosh \Gamma l} & 1 - \frac{\cosh \Gamma x}{\cosh \Gamma l} \end{bmatrix}$$

(2.14)

In the perfect bonding case where there is no shear, $\Gamma \to \infty$, and the strain in the structure and in the PZT will be the same,

$$s_{induced} = \frac{s_{free}}{1 + \psi}$$

(2.15)

To check whether the shear lag solution is needed, the actual strain distribution for the worst case among all the samples was calculated using (2.14). The worst case was a sandwich with 60 mil Aluminum plates and thickness of one bonding layers of 0.7 mil with shear modulus of the epoxy of about 2 GPa. The resulting relative stiffness is 12.16 and the shear lag parameter is 3516.5 m$^{-1}$. The normalized strain distribution is shown in Figure 2-9. It can be seen that the normalized strain in the structure rapidly approaches 0.076, the value given by the perfect bonding solution. Only for the area within about 15 times the bonding layer thickness from the edge does the strain deviate from the value given by (2.15). Thus solution for the perfect bonding case will be used for the rest of the comparisons.

---

4 An exact shear modulus was unavailable from the manufacturer. However, the figure used here is representative of a typical epoxy taken from Reference 61.
Figure 2-9. Plot of strain distribution along the length of the sandwich structure due to shear lag. This represents the worst case among all the sandwich structures, with $\psi=12.16$ and $\Gamma=3516.5$ m$^{-1}$.

It is important to recognize the limitation of this one-dimensional analysis. First, the sandwich structure is really a two-dimensional plate structure. There are some physical effects, such as the Poisson's effect, that the one-dimensional analysis cannot capture. The solution in (2.14) is only valid for cross sections of the sandwich near the center. As the location of the cross section approaches one of the corners or edges, the solution in (2.14) will diverge from the actual strain in the structure. However, since the strain gages were mounted on the center of the sandwich, such effect is negligible. Another limitation of this analysis is that shear effects in the ceramic or the substrates are completely ignored. For structures that have high stiffness or small thickness, such effect should be insignificant. However, if either of these cases are true, or the strain near an edge is considered, material shear can become important [4, p.81].

By using the free strain data and (2.15), the actuation strain assumption prediction was computed for each group of sandwiches. Comparisons are done at six different field levels, identical to the field levels used in Figure 2-7. The results are shown in Figure 2-11 to 2-15 for $\psi$ at 0.46, 0.61, 4.05, 8.11, and 12.16, respectively. For clarity of presentation, the following parts of this thesis will refer to different parts of the butterfly loop as labeled in Figure 2-10. It can be seen that for all cases, the actuation strain assumption overpredicts
the induced strain in the structure. As the mechanical restraint on the PZT increases, the discrepancies also increase dramatically. In the most extreme cases, the prediction is over twice the actual induced strain throughout the whole strain history.

![Figure 2-10: The labels for different parts of the butterfly loops. A is where the applied field vanishes. B is where the applied field is maximum. C is edge of the butterfly where polarization reversal is occurring. D is the location of the coercive field, where polarization reversal starts. E is the region where large nonlinearity starts to occur when the applied field opposes the direction of the polarization.](image)

In addition to the discrepancies in the strain level, there are also fundamental differences between free and stressed cases. First, the amount of hysteresis exhibited by the actuator decreases with increasing stress. The most visible changes in this respect occurred at low field levels, before polarization reversal took place. In the case of the most restraint, the amount of hysteresis observed in the strain history is almost nil compared to the peak to peak strain. The second difference is in the shape of the butterfly loop. The inner edges of the butterfly loop, region E, of the clamped samples are visibly more straight than that of the free samples. As the amount of clamping increases, this effect becomes more prominent. One possible explanation to this effect is that as the amount of stress in the ceramic increases, the polarization in the lattice is force to stay in its original position longer, resulting a linearizing effect in the material behavior. This argument also agrees with the decrease of hysteresis in the material. Massive polarization reversal occurs throughout the ceramic once the coercive field is reached, unlike the more gradual progression into polarization reversal in the less clamped cases. This leads to the third observation, that the value of coercive field, i.e., the location D, in all the clamped cases remain quite constant. Thus, clamping in the transverse direction does not affect the
occurrence of polarization reversal. This can be further confirmed by a comparison of the hysteresis loops for electrical displacement made in Figure 2-16 after full reversal was achieved. It can be seen that mechanical loading perpendicular to the poling axis has no major effect on the electrical displacement in the poling direction. The insensitivity of polarization in the poling direction to lateral stresses is consistent with earlier observations [14]. Moreover, the failure of the actuation strain assumption is quite apparent in all the clamped cases. Thus, the result of this experiment firmly concludes that the actuation strain assumption cannot adequately model the induced strain on a structure produced by ferroelectric actuators.
Figure 2-11. Comparison of actual strain level and predictions from actuation strain assumption for $\psi=0.46$. The peak applied field is 0.3 Hz, with amplitude (a) 472.4 V/mm, (b) 629.9 V/mm, (c) 708.7 V/mm, (d) 787.4 V/mm, (e) 866.1 V/mm, and (f) 944.9 V/mm. The points are the experimental strain data, and the dotted lines are the predictions of the actuation strain assumption.
Figure 2-12. Comparison of actual strain level and predictions from actuation strain assumption for $\psi=0.61$. The peak applied field is 0.3 Hz, with amplitude (a) 472.4 V/mm, (b) 629.9 V/mm, (c) 708.7 V/mm, (d) 787.4 V/mm, (e) 866.1 V/mm, and (f) 944.9 V/mm. The points are the experimental strain data, and the dotted lines are the predictions of the actuation strain assumption.
Figure 2-13. Comparison of actual strain level and predictions from actuation strain assumption for $\psi = 4.054$. The peak applied field is 0.3 Hz, with amplitude (a) 472.4 V/mm, (b) 629.9 V/mm, (c) 708.7 V/mm, (d) 787.4 V/mm, (e) 866.1 V/mm, and (f) 944.9 V/mm. The points are the experimental strain data, and the dotted lines are the predictions of the actuation strain assumption.
Figure 2-14. Comparison of actual strain level and predictions from actuation strain assumption for \( \psi = 8.11 \). The peak applied field is 0.3 Hz, with amplitude (a) 472.4 V/mm, (b) 629.9 V/mm, (c) 708.7 V/mm, (d) 787.4 V/mm, (e) 866.1 V/mm, and (f) 944.9 V/mm. The points are the experimental strain data, and the dotted lines are the predictions of the actuation strain assumption.
Figure 2-15. Comparison of actual strain level and predictions from actuation strain assumption for $\psi=12.16$. The peak applied field is 0.3 Hz, with amplitude (a) 472.4 V/mm, (b) 629.9 V/mm, (c) 708.7 V/mm, (d) 787.4 V/mm, (e) 866.1 V/mm, and (f) 944.9 V/mm. The points are the experimental strain data, and the dotted lines are the predictions of the actuation strain assumption.
2.3 CONCLUSIONS

In this chapter, the experimental aspect of the study was discussed. First, a series of resonance tests was done on PZT–5H disks to obtain some of the material constants of the ceramic. These experiments would test the consistency of quality among the wafers, as well as to verify the accuracy of the values supplied by the manufacturer. Due to constraint on the geometry of the specimens, only $\varepsilon_{33}^T$, $s_{i1}^E$ and $d_{31}$ of the ceramics were measured. Even taking into account the uncertainties in measurement and instrumentation, it was found that the measured values of these material constants are in extremely good agreement with the manufacturer's figures.

The second series of experiments were carried out on sandwich structures, with PZT wafers in the center as actuators. The strain and electrical displacement of the PZT were monitored as voltage was applied until polarization reversal occurred. To verify that the strain measurements from the strain gages on the surface of the structures are representative of the strain of the PZT, the bonding layers were treated as a shear a layer, and a shear lag analysis was carried out. The analysis revealed that for the thicknesses of
the bonding layers measured in the sandwich structures, the strain gage measurements of the structural strain will indeed be very close to the strain in the PZT.

From the known strain history of an unconstrained PZT wafer and the relative stiffness of the structure, the actuation strain assumption can be used to predict the induced strain of the structure. The predictions were compared to the actual experimental results at five different levels of clamping. The results showed that the predictions from the actuation strain assumption consistently overpredicted the induced strain level, almost by a factor of two in the extreme cases. Thus, it is concluded that the actuation strain assumption is unsuitable to be used for strain prediction, especially in cases when the induced stress in the actuator is high.

There are several important aspects of the qualitative behavior of the PZT under stress. First, it was found that the field–strain behavior differ significantly from the stress-free case. In all cases, amount of hysteresis observed decreases with increasing stresses. Furthermore, as the amount of clamping increases, the field–strain relationship before reversal straightened considerably. This observation indicates that the material nonlinearity is closely related to the geometry of the lattice. As larger stresses are applied, the mobility in the lattice decreases, and force the material to behave closer to a linear material prior to reversal. This type of behavior should be able to be describe by an accurate model of polarization in the lattice. Second, it was observed that the dielectric behavior of the PZT in the poling direction is not affected by the applied stresses in the other two directions. The observed hysteresis loops in all cases are basically the same in shape and magnitude. Third, the point at which polarization reversal occurs, i.e., the coercive field, remain quite constant in all cases. Finally, the amount of actuation strain produced decreases with applied stresses. The multiple-family model must be able to reproduce these effects for it to be useful.
Chapter 3: Formulation of Ferroelectric Ceramics Model

As stated in the previous chapters, a model with multiple families of internal variables will be developed to model ferroelectric ceramics. Such a model will exploit the random nature of ceramic grain structures to fully describe the process of polarization reversal in the ceramic under both large electric field and high stress. The model derived in this chapter is based on the development in Reference 62. The construction of the model may be divided into three steps. The first step is to understand the fundamental behavior of a single crystallite under the influence of an electric field and a mechanical stress. Then the simplest possible phenomenological model is formulated to capture the mechanics of polarization reversal at a microscopic level. The second step is to model a ferroelectric ceramic as a body composed of a large number of these crystallites that are oriented in a random fashion. In addition, certain crystallite properties are modeled with statistical distributions that reflects nonuniformities among crystallites. The final step is to use the responses of all crystallites to calculate the macroscopic response of the ceramic. Two methods are developed to accomplish this task. The first method is to directly average all the crystallite responses. The second method is to use a set of series expansions of the macroscopic responses. First, some general assumptions have to be made to define scope of the model and also to discuss the limitations imposed by these assumptions.

3.1 MODEL ASSUMPTIONS AND LIMITATIONS

Most of the important properties of ferroelectrics in general were discussed in §1.1. It is obviously quite impossible to model such a wide range of behaviors with a single model. To further guarantee usability, enormous simplifications must be made to limit the complexity of the model. Moreover, an overly general model is usually not required in engineering applications. The key feature of the model is its ability to capture the isothermal quasi-static behaviors of ferroelectric ceramics when the applied electric field and stress exceed low magnitude limits. More specifically, the quasi-static behavior of spontaneous polarization in the crystallites of a ferroelectric ceramic is modeled. Since all the macroscopic field variables depend intimately on the state of polarization, a solid phenomenological model of polarization will be sufficient for many engineering purposes.

There are model assumptions on each level of material reality intended to remove many of the unnecessary details and thus simplify the formulation. The first assumption is
that the bulk material considered is polycrystalline in nature and macroscopically homogeneous. Defects such as large pores and cracks are excluded due to the complications introduced in modeling such effects. Second, all the crystallites in the ceramic are assumed to be perfect crystals with only a single ferroelectric domain, have the same size, and have uniform fields inside the crystallite. These assumptions for the crystallites are extremely crude and far from reality. However, they eliminate a multitude of complications. Crystallographic defects and impurities (such as dopants) are no longer required to be dealt with directly. Furthermore, the absence of domain walls in the crystallite eliminates the need to model the dynamics involved in polarization reversal on the scale of a crystallite, resulting in a very simple crystallite model. With the reduction in complexity in the crystallite model, a larger number of internal variables can be utilized, thus providing a closer approximation to the ceramic polycrystalline structure. A severe limitation resulting from this assumption is that many of the rate effects such as aging and domain wall movements are completely absent from the model. For some ceramics such as soft PZTs, the rate effects are very prominent in the return path of a polarization reversal cycle. In those instances, the model predictions are expected to diverge significantly from the real material behaviors. The restrictions that all crystallites have the same size further simplify the model derivations as well as the averaging procedure used to calculate the macroscopic variables of the ceramic from the crystallite variables.

The third assumption is that the lattice structure of the crystallites is tetragonal in the ferroelectric phase, with a cubic perovskite structure in the paraelectric phase; specifically, ferroelectrics with the same structure as barium titanate. The origin of ferroelectricity in this class of materials can be roughly associated with the displacive mechanism of the body center ion, in many cases the titanium ion. Thus this model excludes materials with other types of ferroelectric mechanisms, such as hydrogen bonds. More importantly, almost all the ferroelectrics used as actuators or sensors, such as PZT, belong to this class. The fourth assumption is that individual crystallite behaviors are uncoupled, i.e., the state of a crystallite depends only on its own state and the external loads applied to it. This simplification is obviously not true. In the most simple case, a change of shape of a crystallite due to switching will impress large stresses on its neighbors and affect their behavior. Finally, the ceramic is assumed to be under quasi-static, isothermal conditions, with the ambient temperature far away from Curie point or any type of ferroelectric-ferroelectric phase transition temperatures. Therefore, all the constitutive properties and lattice parameters are constants, rather than functions of temperature. Any kind of anomalies occurring during phase transitions can then be ignored. This simplification
incurs another serious limitation on the resulting model — temperature effects are certainly important in many applications, as well as in manufacturing processes, such as poling.

3.2 IDEALIZED SINGLE CRYSTALLITE MODEL

The first step in constructing a model for a ferroelectric ceramic is to establish a model of the crystallites that make up the ceramic body. This crystallite model will serve as the most basic component of the ceramic model. This model encompasses several features that will characterize its electromechanical responses. The first is a set of linear constitutive relations that quantifies the nominal responses of the crystallite under a given set of electrical and/or mechanical external loads. The second feature consists of the geometric constraints on the possible configurations of spontaneous polarization in the crystallite and the changes in the crystallite responses brought about by a change in the state of the polarization. Finally, there is a rule that governs when the change of state of the spontaneous polarization will occur.

With the assumption that all the crystallites are single-domain perfect crystals, each crystallite can be idealized as a unit cell of the lattice. Materials with a structure similar to that of barium titanate belong to the crystal class of 4mm. The three crystallographic axes are mutually orthogonal, and the material is both elastically and dielectrically isotropic in the cubic phase, due to the high degree of symmetry in the lattice. In addition, there is no piezoelectric activity in this phase. As the temperature decreases and the material enters the tetragonal phase, the material becomes piezoelectric. The crystallographic axes are still mutually orthogonal, but now the lattice has a preferred orientation, which makes it transversely isotropic in both elastic and dielectric properties. The crystallite model will operate in this configuration. First, the crystal frame is defined to be the reference frame that is physically attached to the crystallite. The axes of the crystal frame are denoted by x, y and z. This frame basically represents the relative spatial orientation of the crystallite with respect to the ceramic body, and does not depend on the location of the spontaneous polarization. The origin of the coordinate system is chosen to be the center of the crystallite, with the axes aligned with the crystallographic axes. The z-axis of the crystal frame is chosen to be aligned with the initial polar axis of the lattice.

However, when the spontaneous polarization switches from one location to the other, the preferred direction in the lattice also changes even though there is no physical rotation of the crystallite. For example, when the spontaneous polarization switches from the z-axis to the x-axis, the x-axis becomes the new polar axis, and the material constants will be different from those of the y- and z-axis. To account for such changes in the
calculations, it is necessary to introduce a reference frame that defines the principle directions of the material constants. The direction in which the material properties are different from the other two is defined to be the 3-axis, with the other two axes labeled as the 1- and 2-axis. This is the local material constant frame, which will also be denoted as the 123-frame. This frame is used to describe the material properties of the crystallite. In the tetragonal lattice, the spontaneous polarization can reside in any of the six possible directions that are aligned with the crystallographic axes. As the direction of the polarization changes, the local material constant frame also changes to follow the new polarization direction. Thus, the material constants remain unchanged in this frame. The relations between the orientations of the crystal frame and the 123-frame is illustrated in Figure 3-1 for all possible configurations of polarization in the lattice.

![Diagram](image)

Figure 3-1. The relations between the orientation of the 123-frame and the crystal frame for all six different locations of polarization; (a) through (f) represent the polarization to be along z, x, y, -z, -x, -y axis, respectively.

With the definition of these two reference frames for the crystallite, a reference state which serves as the initial state of the polarization can be defined. The reference state of the crystallite is defined to have the polarization in the positive z-direction of the lattice. In other words, the 3-axis is aligned with the z-axis in the reference state. Initially, when there are no external stimuli, the crystallite is in the reference state. As shown in Figure 3-2, the dimension of the crystallite in the direction of the polarization is longer than the other two by the factor $\frac{c}{a}$, which is specific to the particular composition.
3.2.1 Constitutive Relations for Crystallite

With the above definitions of coordinate systems, the constitutive relations of the crystallite can be developed. The choice of independent variables in this case is the complementary variables, mechanical stress and electric field, and the observed responses are their conjugate variables, strain and electrical displacement. There are three different contributions to the strain and electrical displacement, and they can be written as,

\[
S_{ij}^{total} = S_{ij}^{mech} + S_{ij}^{piezo} + S_{ij}^*,
\]
\[
D_{i}^{total} = D_{i}^{diele} + D_{i}^{piezo} + D_{i}^*.
\]

Quantities with superscript * denote the contributions due to the existence of the spontaneous polarization. By assuming that the crystallite is a linear piezoelectric body that can be described by the linear theory discussed in §1.2.2, (3.1) can be expanded into

\[
\begin{align*}
(S_{ij}^{total} - S_{ij}^*) &= s_{ijkl} T_{kl} + d_{mij} E_m, \\
(D_{i}^{total} - D_{i}^*) &= d_{ijk} T_{jk} + \varepsilon_{ij}^* E_j.
\end{align*}
\]

(3.2)

Alternately, the stress and strain can be cast into Voigt notation, so that (3.2) becomes a set of matrix equations.
\[
\begin{align*}
(S_i^{\text{total}} - S_i^e) &= s_{ij}^E T_j + d_{kl} E_k, \\
(D_i^{\text{total}} - D_i^e) &= d_{ik} T_k + e_{ij}^T E_j,
\end{align*}
\] (3.3)

where engineering strains are used instead of the tensor strains. The convention for the indices is as follows,

\begin{align*}
S_1 &= S_{xx}, & S_2 &= S_{yy}, & S_3 &= S_{zz}, & S_4 &= 2S_{yz}, & S_5 &= 2S_{xz}, & S_6 &= 2S_{xy}, \\
T_1 &= T_{xx}, & T_2 &= T_{yy}, & T_3 &= T_{zz}, & T_4 &= T_{yz}, & T_5 &= T_{xz}, & T_6 &= T_{xy}.
\end{align*}

Voigt notation simplifies the constitutive relations by exploiting the inherent symmetry in the higher order tensors. From this point on, all derivations will be based on the vector form in (3.3) rather than the tensor form in (3.2), unless otherwise stated.

Since all the material constants are expressed in the 123-frame, whereas all the field variables are expressed in the crystal frame, when the two frames do not coincide, additional rotations of the material constants are needed to make (3.3) consistent with the crystal frame. The constitutive relations are thus modified as follows.

\[
\begin{align*}
(S_i^{\text{total}} - S_i^e) &= R_i^{t^{-1}} s_{kl}^E R_{ij} T_j + R_{mn}^{t^{-1}} d_{mn} R_{np}^e E_p, \\
(D_i^{\text{total}} - D_i^e) &= R_i^{t^e} d_{kl} R_{im} T_m + R_{mn}^{t^e} e_{np}^T R_{pq}^e E_q,
\end{align*}
\]

where \( R^t, R^t^1 \) and \( R^e \) are the rotation matrices that relate the strain vector, the stress vector and the electric field vector in the 123-frame and the crystal frame,

\[
T_i' = R_i^t T_j, \quad S_i' = R_i^t S_j, \quad E_i' = R_i^e E_j.
\]

\( T_i', S_i' \) and \( E_i' \) are the stress, strain and electric field expressed in the 123-frame, and \( T_i, S_i \) and \( E_i \) are in the crystal frame. Thus, \( R^t \) and \( R^t^1 \) are 6×6 matrices, whereas \( R^e \) is a 3×3 matrix. Because of the orthogonality of the crystallographic axes, the two frames always differ by some combinations of 90° rotations, making all three rotation matrices populated by only 1’s and 0’s. The rotation matrices for stress and strain used in this case is not a proper rotation; in fact they are derived from a set of tensor rotations, which can be written as similarity transforms on the stress and strain matrices. Thus, these rotation matrices do not have the orthonormal property of other rotation matrices such as \( R^t \). To simplify notation further, define

\[
\begin{align*}
s_{ij}^E &= R_i^{t^{-1}} s_{kl}^E R_{ij}^t, \\
n_{lm} &= R_i^{t^e} d_{kl} R_{im}^t, \\
e_{ij}^T &= R_i^{e} e_{np}^T R_{pq}^e.
\end{align*}
\]

\footnote{Even though both stress and strain are second order tensors, \( R^t \) and \( R^t^1 \) are not the same. This is due to the definition of shear strains in the Voigt notation which includes an extra factor of 2.}
By using these definitions, the constitutive relations can be written as

\[
\begin{align*}
\left( S^\text{total}_i - S^*_i \right) &= \tilde{S}_{ij}^* E_j + \tilde{d}_{pi} E_p, \\
\left( D^\text{total}_i - D^*_i \right) &= \tilde{\varepsilon}_{im}^* T_m + \tilde{\varepsilon}_{iq}^* E_q.
\end{align*}
\] (3.4)

For external loads that are fairly small, the spontaneous polarization in the crystallite does not switch, or undergo a change of direction; thus it stays in the reference state. In this case, the contributions from the spontaneous polarization are

\[
S^*_i = 0, \quad D^* = \begin{bmatrix} 0 \\ 0 \\ P_s \end{bmatrix}.
\] (3.5)

Following these definitions, the reference state will have zero strain, but non-zero electrical displacement in the absence of external loads. The reason for this choice lies in the difference in nature between strain and electrical displacement. In a single crystallite system, the definition of a zero strain state does not affect the results of the derivation. However, in a multiple crystallite system, any other definition will imply a certain contradiction to common sense. At this point, the source of this contradiction is not apparent, since it will depend on the construction of the ceramic model in §3.3. However, if the strain associated with the spontaneous polarization is defined to be non-zero in the reference state, it can be shown that one can construct a ceramic system with isotropic material properties and no remanent polarization, but a non-zero remanent strain. This will correspond to the situation that the virgin state of the ceramic is not strain-free in the absence of external loads. Although a consistent model can still be derived based on this alternate definition, the physical results can become quite counterintuitive. By using (3.5), such awkward situation can be avoided.

When the external load is sufficiently large, the polarization can undergo a change of direction depending on the sense of the load. Because of the orthogonal crystallographic axes, the crystallite in general can undergo two types of switching, namely 180° or 90° switching. The type of switching is related to the destination of the polarization with respect to the crystal frame, but not to the relative rotation of the polarization. When the polarization settles in the negative z-direction, the crystallite experiences a 180° switching; polarization in the crystallite is rotated by 180° from the reference state, and the size of the

---

2 The simplest system that such situation can happen is a two-crystallite system. Both crystallites are in reference state but are oriented in opposite directions. With all the crystallites in the reference state, the system is by definition in the virgin state. The remanent polarization in this case is clearly zero. However, if the remanent strain associated with the reference state in the crystallites are defined to be non-zero, this system will have some non-zero strain in the virgin state.
crystallite remains the same. Thus, there will be a sign change in $D^*$, but there will be no net strain associated with the switching of polarization into this anti-parallel state.

On the other hand, if the external loads are applied in such a way that the polarization settles into any of the other directions that are orthogonal to $z$-axis, the crystallite then experiences $90^\circ$ switching. In this scenario, the polarization is rotated by $90^\circ$ from the reference state, and brings about a net change in the dimensions of the crystallite. Since the new polar axis is orthogonal to the original direction, the crystallite will elongate along this new polar axis and contract in the $z$-direction. The components of strain and electrical displacement associated with each of the six polarization configurations are summarized in Table 3-1.

Table 3-1. Summary of components of strain and electrical displacement due to direction of the spontaneous polarization in the crystallite.

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$-x$</th>
<th>$-y$</th>
<th>$-z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1^*$</td>
<td>$c/a - 1$</td>
<td>0</td>
<td>0</td>
<td>$c/a - 1$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$S_2^*$</td>
<td>0</td>
<td>$c/a - 1$</td>
<td>0</td>
<td>0</td>
<td>$c/a - 1$</td>
<td>0</td>
</tr>
<tr>
<td>$S_3^*$</td>
<td>$1 - c/a$</td>
<td>$1 - c/a$</td>
<td>0</td>
<td>$1 - c/a$</td>
<td>0</td>
<td>$1 - c/a$</td>
</tr>
<tr>
<td>$S_4^*$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$S_5^*$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$S_6^*$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$D_1^*$</td>
<td>$P_s$</td>
<td>0</td>
<td>0</td>
<td>$-P_s$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$D_2^*$</td>
<td>0</td>
<td>$P_s$</td>
<td>0</td>
<td>0</td>
<td>$-P_s$</td>
<td>0</td>
</tr>
<tr>
<td>$D_3^*$</td>
<td>0</td>
<td>0</td>
<td>$P_s$</td>
<td>0</td>
<td>0</td>
<td>$-P_s$</td>
</tr>
</tbody>
</table>

Note that $S^*$ is the same regardless of whether the polarization is pointing in positive or negative directions. Since all the possible directions for the polarization are aligned with the edges of the lattice in the tetragonal phase, there will be no shear strains involved with any $90^\circ$ switching. The strain in Table 3-1 depends only on the particular direction the polarization is switched, and does not depend on the history of polarization. It should also be noted that volume of the crystallite is preserved under this definition of $90^\circ$ switching. By using these definitions of $S^*$ and $D^*$, the elastic and electrical responses of the crystallite can be calculated directly from (3.3).
3.2.2 Switching Rule

The last part of the crystallite model is to postulate a rule which governs the switching of polarization based on the geometry and constitutive relations defined above. To derive the criterion for determining the switching of polarization and the direction it switches into for any arbitrary external electrical and mechanical load, the principle of minimum potential energy is applied. The principle states that the natural displacement of a system minimizes the total potential energy,

$$\Pi = U - W^{\text{switch}},$$ (3.6)

where $U$ is the internal potential energy and $W^{\text{switch}}$ is the work done by the electrical and mechanical external load. The exact form of these two terms will be presented in the latter part of this section. However, in the case of polarization reversal, a switching will only occur when the work done by the external loads due to switching actually exceeds the internal energy barriers which inhibit switching. This means that first, switching of polarization will only occur when the total potential energy is negative, i.e., $\Pi < 0$. Second, when there are multiple locations where this criterion is satisfied, the polarization will settle into the location where $\Pi$ is minimum. Since there are only five other possible switching locations at any one time, $\Pi$ can be calculated for all the possible sites for a set of given loads. Then a search can be used to find the one that satisfies both criteria.

The work term in (3.6) represents only the work done by the external load when a switch occurs. This does not include the actual work done by the external load that is stored as elastic and electrical energy in the crystallite. In other words, $W^{\text{switch}}$ is the work done by the external loads to cause a permanent mechanical and electrical deformation in the crystallite which is thermodynamically irreversible. Thus, only $S^*$ and $D^*$ contribute to $W^{\text{switch}}$. Calculating the work done by the external loads is straightforward. In general, the total work done contains contributions from both electrical and mechanical loads:

$$dW = \oint_{B_\nu} \left( F_i du_i - \rho d\varphi \right) dA$$ (3.7)

where $F$ and $u$ are the external force and the displacement on the surface of the crystallite, respectively, $\varphi$ is the electrical potential of the applied electric field, and $\rho$ is the charge density on the crystallite surface. The integral is carried out over the surface of the crystallite. Assuming that there is a certain constant displacement and charge configuration in the body when there is no external load, a work function can be integrated from (3.7). Furthermore, by introducing the stress tensor and electrical displacement, where,

$$F_i = T_{ij}n_j, \quad \rho = D_in_i,$$
with \( n_i \) as the unit outward normal, the work term can be simplified as follows using the Divergence Theorem.

\[
W = \iiint_{V} (F_i u_i - \rho \phi) dA - W_o.
\]

\[
= \iiint_{V} (T_{ij} u_i - \phi D_j) n_j dA - W_o,
\]

\[
= \iiint \text{div}(T_{ij} u_i - \phi D_j) dV - W_o. \tag{3.8}
\]

By invoking the equilibrium condition of the applied stress, \( T_{ij,j} = 0 \), and the assumption that there are no free charges in the crystal, \( D_{j,j} = 0 \), the expression is further simplified to

\[
W = \iiint (T_{ij} u_{i,j} + E_k D_k) dV - W_o. \tag{3.9}
\]

The expression in (3.8) is the work done by external loads to change the crystallite from some unknown initial configuration into a particular polarization state. The actual value of \( W_o \) is not important, as it is only an offset to all the work terms. Now that \( W \) only depends on the direction of the spontaneous polarization, (3.5) and the components in Table 3-1 can be substituted into (3.9). The electrical displacement is simply equal to \( D^s \). Furthermore, all potential sites for spontaneous polarization in the crystallite are orthogonal; the displacements are always aligned with the crystal frame. Thus, the displacement gradient \( u_{i,j} \) is always diagonal, and is equal to \( S^s \) after (3.9) is written in Voigt notation,

\[
W = \iiint (T_1 S^s_1 + T_2 S^s_2 + T_3 S^s_3 + E_1 D^s_1 + E_2 D^s_2 + E_3 D^s_3) dV - W_o. \tag{3.10}
\]

Furthermore, by applying the uniform field assumption, the (3.10) can be simplified to,

\[
W = (T_1 S^s_1 + T_2 S^s_2 + T_3 S^s_3 + E_1 D^s_1 + E_2 D^s_2 + E_3 D^s_3) V_c - W_o, \tag{3.11}
\]

where \( V_c \) is the volume of the crystallite. Then the work done by the external load in switching the polarization from any initial state to any final state is given by,

\[
W_{\text{switch}} = W_{\text{final}} - W_{\text{initial}},
\]

\[
= (T_i (S^s_i|_{\text{final}} - S^s_i|_{\text{initial}}) + E_i (D^s_i|_{\text{final}} - D^s_i|_{\text{initial}})) V_c. \tag{3.12}
\]

The internal potential energy term that is involved in polarization reversal (not the same as the internal energy composed of strain energy and electrical energy stored) however, cannot be evaluated explicitly as it cannot be expressed in any analytical form. Furthermore, even if one can derive \( U \) analytically, it will have a complicated dependence on the lattice parameters and the exact thermodynamic states of the crystallite. Fortunately, for the purpose of this derivation, the only important property of \( U \) that is needed to determine switching is the size of the energy barrier. Thus, \( U \) will be assigned a constant numerical value. For 180° switching, since there is no net strain in the crystallite, there will
only be an electrical energy barrier, $U_p$. However for 90° switching, there will be both a mechanical and electrical energy barrier, $U_m$ and $U_d$, respectively. When the polarization is to switch into a direction aligned with either x- or y-axis from the original polar axis, the external work will have to overcome the sum of the two barriers for the switching to take place. Inside the actual ceramic, where the crystallites are bound by neighbors, there will be additional complications in the switching rules. This is because as the crystallite switches and changes shape, free expansion is no longer possible. Consequently, some strain energy is stored in the surrounding medium. Necessary modifications for such situations will be addressed in §3.3.2.

The existence of internal energy barriers is not implicit to (3.6), but rather a character of the ferroelectric crystallite. The essence of hysteresis is entirely captured by the shape of the internal potential energy function $U$. For an ordinary linear elastic body, or dielectric body, $U$ has a single global minimum, and its shape is usually parabolic. In these cases, hysteresis cannot exist since there is only one equilibrium state. For hysteresis of any sort to exist, as in the case of ferroelectrics, there must be multiple local minima in $U$. The consequence of multiple minima is the existence of one or more local maxima, which represent the energy barriers that prohibit the system from moving into an alternate equilibrium state in the absence of external loads. This internal energy is completely parallel to the one discussed in §1.2.3, except that the complete $U$ must now be defined in three dimensional space, and has six minima in this case, which is the basic difficulty involved in finding an analytical expression for the internal potential energy related to polarization reversal. If more details are known about $U$, it is possible to obtain more information about the behavior of the crystallite during the course of switching. However, the complexity of the crystallite model will also increase.

### 3.3 CERAMIC MODEL

Since a ceramic is an aggregate of crystallites, the material state of the ceramic can be captured from the group of polarization states of all the crystallites. With the crystallites distributed in random orientations, the crystal model constructed in the above section can be used to determine the responses of all the crystallites and thus characterize the complete state of the ceramic. There are two steps involved in extending and modifying the idealized single-crystal model to a ceramic model. First, the orientations of the crystallites are completely random within the ceramic, i.e., the probability of a crystallite possesses any orientation is equal. This can be modeled by a group of crystallite which are uniformly
oriented in all directions in three dimensions. This distribution of crystallite orientation not only has to capture the random fashion of crystallite arrangement, but also demonstrate the existence of a nonpolar initial state that is representative of the virgin state in the ceramic. Second, since the crystallites in a ceramic are physically different, and are under different conditions due to defects, dopants, intergranular charges and stresses, the energy barriers will vary in each crystallite. Since there is no analytical means of accounting for all these effects, the barriers will be modeled as a set of random variables.

![Diagram](image)

**Figure 3-3.** The relation between the global ceramic frame and the crystal frame. \( \theta, \phi, \psi \) are the Euler angle for that particular crystal frame.

Before the formulation of the ceramic model can begin, an additional reference frame must be introduced. The *global ceramic frame* is defined to be fixed with respect to the ceramic body. This is the frame from which the absolute orientations of the crystal frames are defined. The orientation of any crystallite, which is characterized by orientation of its crystal frame, can be distinctly represented by a set of three Euler angles, \( \phi, \theta, \) and \( \psi \), as illustrated in Figure 3-3. Any physical quantities in the global frame, such as stress and electric field, can be transformed into any given crystal frame by three successive rotations (tensors, however, have different transformation rule than vectors). Since rotations in three dimensions do not commute, the order of rotations must be first established. To transform from the global frame to the crystal frame, where the polar axes are aligned, the first rotation of \( \theta \) is about \( Z \)-axis, then the second rotation of \( \phi \) away from
the Z-axis (the axis of rotation is actually the y-axis of the first rotated frame), and finally, a rotation of \( \psi \) about the z-axis must be performed. The transformation from the local frame back to the global frame will involve an inverse rotation of \( \psi \), then \( \phi \), and finally \( \theta \). The three rotation matrices and the total rotation matrix are,

\[
R_\theta = \begin{bmatrix}
\cos \theta & \sin \theta & 0 \\
-\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{bmatrix}, \\
R_\phi = \begin{bmatrix}
\cos \phi & 0 & -\sin \phi \\
0 & 1 & 0 \\
\sin \phi & 0 & \cos \phi
\end{bmatrix}, \\
R_\psi = \begin{bmatrix}
\cos \psi & \sin \psi & 0 \\
-\sin \psi & \cos \psi & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

\[
R = R_\psi R_\phi R_\theta.
\]

where \( R \) is the complete rotation matrix. All of the above rotation matrices are orthonormal matrices, i.e., the inverse of the rotation matrix is its own transpose. In addition, the determinant of all the rotation matrices are equal to 1. The transformation rule for any external electric field and mechanical stresses applied to the ceramic are,

\[
E_{local} = RE_{global}, \quad \text{(vector transformation)}
\]
\[
T_{local} = RT_{global} R^T. \quad \text{(tensor transformation)}
\]

(3.14)

The tensor representation of stress in terms of the stress components in Voigt notation is as follows,

\[
T = \begin{bmatrix}
T_1 & T_6 & T_5 \\
T_6 & T_2 & T_4 \\
T_5 & T_4 & T_3
\end{bmatrix}
\]

From these relations, the load felt by the crystallite due to the external load can be calculated\(^3\). Similarly, the resultant strain and electrical displacement of the crystallite in the crystal frame can be transformed into the global frame by using the inverse transforms.

---

\(^3\) In this calculation the loads experienced by the crystallites are assumed to be equivalent to the macroscopic external loads. This is obviously a gross simplification. The actual loads on the crystallite should be calculated as in Reference 63.
3.3.1 Ceramic Configuration

One important component of the ceramic model is to arrange the group of randomly oriented crystallites in a meaningful manner in order to accomplish two goals. The first goal is to be able to construct an initial state for the ceramic model which corresponds to the virgin, unpolarized state of the ceramic with all the crystallites in the reference state. The second goal is ensure that such a configuration will indeed encompass all the possible orientations which can exist and each orientation can be uniquely addressed by the set of three Euler angles\(^4\).

The first step of the construction is to determine the range of the Euler angles that will be needed to satisfy the uniqueness requirement. If only the first two Euler angles, \(\theta\) and \(\phi\), are considered, it is immediately apparent that they are the two angular variables in spherical coordinate. By convention, \(\theta\) and \(\phi\) with ranges \((0,2\pi)\) and \((0,\pi)\), respectively, will cover any point on the surface of a sphere, without overlapping regions. To completely capture all the possible crystallite orientations, an additional distribution over \(\psi\) needed. In the most general case, with no additional information about the crystallite, the normal range of \(\psi\) will be \((0,2\pi)\). However, since the crystallite has three mutually orthogonal crystallographic axes, only a range of \((0,\frac{\pi}{2})\) is needed. Any rotation of \(\psi\) beyond \(90^\circ\) does not yield any new configurations.

With the range of Euler angle established, the distribution of crystallite orientation can be constructed. The simplest configuration that will satisfy all the criteria is to apply (3.13) over the entire range Euler angles in defining the crystal frames. In other words, for a crystallite located at \((\theta_1, \phi_1, \psi_1)\), its crystal frame is defined in terms of the global frame by the total rotation matrix in (3.13),

\[
\begin{bmatrix}
  x_1 \\
  y_1 \\
  z_1
\end{bmatrix} = R(\theta_1, \phi_1, \psi_1) \begin{bmatrix}
  X_1 \\
  Y_1 \\
  Z_1
\end{bmatrix},
\]

where \(x_1, y_1,\) and \(z_1\) are the component of a vector in the crystal frame, \(X_1, Y_1,\) and \(Z_1\) are the components in the ceramic frame. This distribution of crystallites is completely uniform over the surface of a sphere with unit radius, with the \(z\)-axis of the crystal frame aligned with the unit outward normal at that point on the surface. This arrangement also satisfies the virgin state requirement. When all the crystallites are in the reference state, all spontaneous polarization vectors are pointing along the unit outward normal of the sphere.

---

\(^4\) It is important to note that discretization of the Euler angles is unavoidable in implementing the model. This certainly will not cover all possible orientations. However, the goal here is to ensure that the established system can uniquely address all the possible configurations in the original, continuous representation.
The resultant net polarization of the system obviously vanishes. In addition, the resultant
strain of the system is also zero due to definitions in (3.5).

Although some of the conventions of spherical coordinates are used to construct
this crystallite arrangement, there is no spatial information implied in the construction.
Clearly, the radial variable never enters the construction. This arrangement is only used to
convey information about the orientations of the crystallites, but not the actual physical
location of the crystallite in the ceramic. Even the sphere with unit radius is only a
convenient tool to aid the visualization of the crystallite configuration.

3.3.2 Energy Barriers in the Ceramic Model

In this section, the energy barriers of the crystallites in the ceramic model are constructed.
Crystallites in a real ceramic not only differ in the orientation of their crystallographic axes,
their physical states and surrounding conditions are also different. Some obvious physical
differences are their shapes, sizes, and defects. Other effects such as intergranular charges
and stresses induced by neighboring crystallites also come into play. All these factors will
change the internal energy levels as well as the equilibrium states of the crystallites. For
instance, a certain charge distribution on the surface of a crystallite will favor certain
directions for the spontaneous polarization. However, it is impossible to know exactly the
kind of condition that each crystallite is under. Even if these conditions are known, it is still
unrealistic to model them directly due to the complexity involved. One way to deal with
this situation to treat the crystallite properties as random variables. The advantage in this
approach is that only a small number of parameters are needed to specify a statistical
distribution. Thus, the model can be simplified considerably while maintaining certain
variations in crystallite properties.

The most straightforward way to implement this idea is to model all the crystallite
properties as random variables. However, this approach is unnecessarily complicated, and
it also violates the model of the assumptions that all crystallites have same sizes and
composition. Quantities such as the constitutive properties, spontaneous polarization, and
$\gamma / a$ are well defined for a given composition. Thus, the only parameters available to be
modeled as random variables are the energy barriers. There are three energy barrier
quantities associated with each crystallite, $U_p$, $U_d$, and $U_m$. Assuming that their values are
normally distributed in the population of the crystallites, the distribution for each of the
energy barrier can be completely specified by a mean and a variance. Thus, they can be
written as the sum of a mean and a stochastic component,
\[ U_p = \langle U_p \rangle + U_p^{rand} n_p, \]
\[ U_d = \langle U_d \rangle + U_d^{rand} n_d, \]
\[ U_m = \langle U_m \rangle + U_m^{rand} n_m, \]  
(3.16)

where \( \langle \cdot \rangle \) quantities denote the mean over the entire population of crystallites, and \( n \)'s are normally distributed independent (uncorrelated) random variables with zero mean and unit variance. The three factors with superscript \( rand \) are the standard deviations of the energy barriers. Thus, the energy barrier properties of the whole ceramic model can be completely characterized by these six independent values.

In §3.2.2, there are two rules about the energy barriers that defined to govern the switching the spontaneous polarization. The first rule is that the total potential energy the work done due to switching, \( W^{\text{switch}} \), must exceed \( U_p \) for a 180° switching to occur. The second rule is that \( W^{\text{switch}} \) must exceed \( U_d + U_m \) for a 90° switching to occur. As mentioned in that section, two additional rules are needed in the ceramic model to account for effects due to presence of neighbors.

The first additional rule is to address the presence of a surrounding ceramic medium. Since the crystallite in a ceramic is surrounded by its neighbors, switching into 90° states will introduce stresses in the surrounding medium. As a result, a fraction of \( U_m \) is stored in the surrounding medium as strain energy. When the polarization switches back to a direction aligned with the z-axis, the external work will not have to overcome the mechanical energy barrier. In addition, a fraction of that strain energy stored is available to help overcome \( U_d \). Thus the overall energy barrier that the external work has to overcome is less than the barrier of switching into a 90° state, and a back-switching may occur at a lower external load level. The second additional rule is that any switching between 90° states will not include \( U_m \) in the energy barrier, so strain energy will not be accumulated indefinitely if continuous switching among 90° states is to occur. Table 3-2 thus summarizes all the energy barriers for switching between any two locations. It is important to note that these values of energy barriers depends on the fact that the model has the geometry described in §3.3.1, i.e., the initial equilibrium states of all the crystallites have polarization in z-direction, the reference state.
Table 3-2. Summary of the total energy barrier for all possible pairs of switching locations, the rows represent current positions and the columns represent potential switching sites.

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$-x$</th>
<th>$-y$</th>
<th>$-z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>0</td>
<td>$U_d$</td>
<td>$U_d - \gamma U_m$</td>
<td>$U_p$</td>
<td>$U_d$</td>
<td>$U_d - \gamma U_m$</td>
</tr>
<tr>
<td>$y$</td>
<td>$U_d$</td>
<td>0</td>
<td>$U_d - \gamma U_m$</td>
<td>$U_d$</td>
<td>$U_p$</td>
<td>$U_d - \gamma U_m$</td>
</tr>
<tr>
<td>$z$</td>
<td>$U_d + U_m$</td>
<td>$U_d + U_m$</td>
<td>0</td>
<td>$U_d + U_m$</td>
<td>$U_d + U_m$</td>
<td>$U_p$</td>
</tr>
<tr>
<td>$-x$</td>
<td>$U_p$</td>
<td>$U_d$</td>
<td>$U_d - \gamma U_m$</td>
<td>0</td>
<td>$U_d$</td>
<td>$U_d - \gamma U_m$</td>
</tr>
<tr>
<td>$-y$</td>
<td>$U_d$</td>
<td>$U_p$</td>
<td>$U_d - \gamma U_m$</td>
<td>$U_d$</td>
<td>0</td>
<td>$U_d - \gamma U_m$</td>
</tr>
</tbody>
</table>
| $-z$| $U_d + U_m$| $U_d + U_m$| $U_p$| $U_d + U_m$| $U_d + U_m$| 0

$\gamma$ is the back-switching parameter that gives the fraction of strain energy stored that is available upon switching out of the 90° states. Therefore, $\gamma$ is always between 0 and 1. For instance, the energy barrier for a crystallite with polarization in the $y$-direction to switch to the negative $z$-direction will be the last element in the second row, which is $U_d - \gamma U_m$.

With these modifications in place, both the energy barriers and the work done on each crystallite in the ceramic model can be calculated at any point in time. Then the electromechanical responses as well as the switching of polarization can be found. The complete material state of the piezoceramic can then be determined.

### 3.3.3 Macroscopic Ceramic Responses

The last component of the model is to determine the macroscopic responses of the ceramic body for a given set of crystallite responses. Since no information about the physical locations of the crystallites is available, it is impossible to postulate a physical method to calculate the macroscopic responses. Two approaches are established to calculate the macroscopic responses from all the crystallite responses. The first method is to use a simple averaging of all the crystallite responses to determine the ceramic responses. The second method is to assume that the macroscopic variables are some arbitrary functions of the external loads and the internal polarization states of the crystallites. A suitable series expansion is then used to calculate the macroscopic responses.

#### Direct Averaging Method

In this method, all the macroscopic quantities are calculated by directly averaging all the microscopic quantities represented in the ceramic frame. For illustration purposes, the
average polarization of the ceramic in the absence of external loads can be calculated as follows. Suppose that each crystallite has the spontaneous polarization in some location, not necessarily in the reference state. Assuming that the crystallites are distributed continuously over the whole range of Euler angles, the distribution of spontaneous polarization in the ceramic frame can be written in terms of the spontaneous polarization in the crystal frame as,

$$P_i(\theta, \phi, \psi) = R_{ji}(\theta, \phi, \psi)D_j^*(\theta, \phi, \psi),$$

where $R_{ji}$ is the inverse transform that maps from crystal frame to global frame, which is the transpose of the total rotation matrix in (3.11). Thus the average polarization is

$$\langle P_i \rangle = \left(\frac{2}{\pi}\right)\left(\frac{1}{4\pi}\right)\int_0^{2\pi} \int_0^{\pi} \int_0^\pi P_i(\theta, \phi, \psi) \sin \phi d\psi d\phi d\theta. \quad (3.17)$$

The constants preceding the integral are normalizing factors. Since the sphere is unit radius, the surface area is $4\pi$. However, to the third integration over $\psi$ requires an additional normalization factor of $\frac{2}{\pi}$, which is the reciprocal of the full range of $\psi$. Thus, if all the crystallites are aligned in the same direction, the average polarization will be equal to $P_i$. It can be easily seen that even if the radius of the sphere is not unity, (3.17) will not be altered, since none of the variables varies with the radius.

Similarly, strain and electrical displacement can be calculated by the same procedure. Before the crystallite responses can be averaged together, first they must be transformed from the their crystal frames to the global frame. The resultant total strain and total electrical displacement in the crystal frame can be rotated into the global frame by using the inverse transforms in (3.12). Thus,

$$D_{\text{global}} = R^T D_{\text{local}}, \quad \text{(vector transformation)}$$

$$S_{\text{global}} = R^T S_{\text{local}} R. \quad \text{(tensor transformation)} \quad (3.18)$$

The strains in (3.18) are tensor strains, and the tensor strain matrix is related to the strain components in Voigt notation as follows,

$$S = \begin{bmatrix} S_1 & \frac{1}{2} S_6 & \frac{1}{2} S_5 \\ \frac{1}{2} S_6 & S_2 & \frac{1}{2} S_4 \\ \frac{1}{2} S_5 & \frac{1}{2} S_4 & S_3 \end{bmatrix}.$$ 

The macroscopic responses of the ceramic can then be obtained by simple component by component averaging of the crystal responses from (3.18). The averages can be written in the integral form in (3.15)
\[
(D_{\text{ceramic}})_i = \left( \frac{2}{\pi} \right) \left( \frac{1}{4\pi} \right) \int_0^{2\pi} \int_0^\pi \int_0^{\pi/2} (D_{\text{global}}(\theta, \phi, \psi))_i \sin \phi \psi d\psi d\phi d\theta, \\
(S_{\text{ceramic}})_{ij} = \left( \frac{2}{\pi} \right) \left( \frac{1}{4\pi} \right) \int_0^{2\pi} \int_0^\pi \int_0^{\pi/2} (S_{\text{global}}(\theta, \phi, \psi))_{ij} \sin \phi \psi d\psi d\phi d\theta. 
\] (3.19)

Using (3.19), to calculate the average electrical displacement of the ceramic body is a very good approximation to the physical system. In nature, electrical displacement represents the flux of charges in the material. Since charge is a scalar quantity, the net charge is the ceramic does not relate to the physical locations of the crystallites. Thus for a prescribed boundary of the ceramic body, the calculation of the total charge flux (average electrical displacement) does not depend on the interconnection structure of the crystallites; it only depends on the net charge in the ceramic. Thus, it can be expected that this averaging method will give very close predictions of the electrical displacement of the ceramic.

On the other hand, calculating the macroscopic strain based on averaging of strains over all families is indeed quite an arbitrary choice which is not motivated by any physical reasons. One can argue that it is far more realistic for one to integrate the strains in each family to obtain the displacement of each crystallite, postulate a way of connecting the crystallites in the ceramic and calculate the gross displacement of the whole system, from which derive the strain of the whole body. While the second method may appear to be a lot more “physically motivated” than the averaging scheme, it is actually just as arbitrary. The reason for this situation lies in the fact that, the ceramic model derived here parameterized the families only by their orientations, but not the physical position of the crystallite in the ceramic body. Thus the question about the interconnection among crystallites never entered the picture of this model. In order for one to use the second method to calculate the macroscopic strain, one still has to arbitrarily choose the interconnection model which adds another level of complexity, without explicitly injecting any more physical information into the model. This severe lack of physical insight in calculating the ceramic strain using (3.19)_2 means that one cannot expect the model predictions of strain to be as satisfactory as the predictions of electrical displacement.

This point precisely ties into the very definition of the zero-strain reference state in (3.5). As pointed out, by utilizing the definition in (3.5), one can avoid having non-zero remanent strain in a virgin ceramic. Now it becomes much more clear that the reason for using (3.5) is only valid when the method of calculating macroscopic strain is based on the crystallite arrangement assumed in §3.3.2 as well as the averaging family strains. If the method of calculating macroscopic strain is changed, (3.5) may also have to be changed accordingly to preserve the zero remanent strain property of the virgin ceramic. Thus it can be seen that even though the derivation of the model can be artificially divided into three
parts, all three are really interrelated in many ways for the ceramic model to be defined properly.

**Series Expansion Method**

This method of calculating macroscopic responses is similar to the approach used in Reference 40. By recognizing the fact that in a poled homogeneous ferroelectric ceramic body, there is net alignment of crystallite polarization only along the poling axis, the amount of computation needed to determine the macroscopic responses can be greatly reduced. Using the notation in Reference 40, the net alignment of crystallites along the poling axis (conventionally assigned to be Z-axis) can be described by two scalar variables, $N^p$, and $N^d$. $N^p$ represents the net alignment of polarization due to crystallites that are polarized in the 180° states, and $N^d$ represents the net alignment of polarization due to crystallites that are polarized in the 90° states. The degree of net alignment is described by the projection of the polarization vector onto the poling axis of the ceramic. Both variables can be evaluated by using the following expression.

\[
N = \left( \frac{2}{\pi} \right) \left( \frac{1}{4\pi} \right)^2 \int_0^{2\pi} \int_0^\pi \int_0^\pi R_{ij} D^i_j(\theta, \phi, \psi) \sin \phi d\psi d\phi d\theta,
\]

(3.21)

where $D^i_j$ is the jth component of the crystallite spontaneous polarization in the crystal frame. However, in the evaluation of $N^p$, only regions with crystallites in 180° states are integrated, and for $N^d$, only regions with crystallites in 90° states are integrated. Due to the additional normalizing factor for $P_T$, if all the crystallites polarization are pointing in the poling axis, then the total alignment will be,

\[
N_T = N_p + N_d = 1.
\]

To use these two variables to calculate the macroscopic responses of the ceramic, both the strain and electrical displacement are assumed to be some arbitrary functions of $N^p$, $N^d$, stress, and field. Thus, they can be written as,

\[
\hat{S}_i(T_k, E_m, N^p, N^d) = 0,
\]

\[
\hat{D}_j(T_k, E_m, N^p, N^d) = 0.
\]

(3.22)

By using a series expansion of the functions in (3.22), the following macroscopic constitutive relations can be reached.

\[
S_i = (s_{ik} + s_{ik}^N |N^i|) T_k + d_{mi} N^i E_m - h_i |N^d|,
\]

(3.23)

\[
D_j = d_{jk} N^i T_k + (\varepsilon_{im} + \varepsilon_{im}^N |N^i|) E_m + k_j N^i.
\]
where $k_1 = k_2 = 0$, $k_3 = P_s$ and $h_4 = h_5 = h_6 = 0$. All other tensors appearing in (3.23) have the appropriate structures similar to piezoelectric material with crystallite structure of 6mm. The only exceptions are $s_{ik}^I$ and $\varepsilon_{im}^I$, which represent the isotropic compliance and dielectric permittivity of an unpoled ceramic. Thus, $s_{ik}^I$ has the isotropic structure and $\varepsilon_{im}^I$ has the structure of an identity matrix. The additional terms with absolute signs do not directly result from the series expansions. These are modifications motivated by physical observations of ferroelectric ceramic behavior. Most of the coefficients in the expansions can be determined directly if a full set of poled material constants and the values of $N^P$ and $N^d$ for such material states are known. Reference 40 describes characterization techniques for this type of models. It is possible to add higher order even terms to the strain equation and odd terms to the displacement equation to fine tune the model behavior. However, such approaches will often result in very cumbersome state equations with a large number of unknown coefficients. Characterization of coefficients for these higher order terms can be very difficult in a three-dimensional system.

With this method, the microscopic responses of the crystallites are no longer required anywhere in the calculation. All the information about the crystallite polarization is buried in $N^P$ and $N^d$. Consequently, for a given applied stress and field, only the switching rule is needed to determine the states of the crystallite polarization and the macroscopic responses. Rotations of crystallite strain and electrical displacement are not required; thus, tremendous saving in computational effort can be achieved. On the other hand, this method is much less fundamental than the direct averaging method. $N^P$ and $N^d$ describe the net projection of all the crystallite polarization on the ceramic poling axis. These two variables are vectorial in nature. Thus, they are unable to capture the tensorial nature of strain. Due to the simplistic treatment of the polarization in the crystallites, the series expansion method is expected to perform worse than the averaging method in the calculation of the macroscopic strain. Consequences of such shortcomings will be investigated in the next chapter.

### 3.4 Thin Plate Ferroelectric Model

The fully three-dimensional ceramic model formulated in the above sections can be generally applied to ferroelectric ceramic with arbitrary geometry with loading. However, when the model is applied to ceramics with simple geometry, such as plates and discs, further simplifications of the model are possible by exploiting geometric symmetry. In order to illustrate the key points in implementing the model, it will be specialized for PZT
ceramics with a thin plate geometry and axial symmetric loading, \emph{i.e.}, with an electric field aligned in \( Z \)-axis through the thickness and with planar stresses in the lateral directions, as shown in Figure 3-4. This model will also be used to compare with some experimental results in the next chapter.

![Figure 3-4. A PZT thin plate with axial symmetric external loads about Z-axis.](image)

The ceramic plate on the \( XY \)-plane is assumed to be completely unpolarized initially. Thus, all elastic and dielectric properties are isotropic, and the ceramic possesses no net electromechanical coupling. In this case, electric field is only applied through the thickness of the plate along the \( Z \)-axis, with \( E_z = E \). The applied stress is only in the plane of the plate, with \( T_{xx} = T_{yy} = T \). Using tensor notation in (3.14), the applied stress and field in this case can be written as,

\[
T^e = \begin{bmatrix} T & 0 & 0 \\ 0 & T & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad E^e = \begin{bmatrix} 0 \\ 0 \\ E \end{bmatrix}.
\]  

(3.24)

In general, both \( T \) and \( E \) can be an arbitrary functions of time. Since both the geometry and the external loads are axial symmetric and the initial state of the ceramic is completely isotropic, none of the variables will depend on \( \theta \). Any two crystallites that differ in orientation in \( \theta \) only will have identical responses. Thus, a collection of crystallites in a slice of the sphere (constant \( \theta \)) is representative of the whole sphere. The rotation matrix that transform the macroscopic stress and field into the crystal frames is only \( R_{\psi}R_{\phi} \). However, the constitutive relations of the crystallites in (3.4) and the switching rule in (3.12) remain unchanged by this simplification.

Both the averaging method and the series expansion method have their simplifications due to the symmetry in the plate. For the averaging method, the modification comes in the rotation matrices in the integrals in (3.19). Since the crystallite
strain and electrical displacement in their crystal frame do not depend on $\theta$, (3.18) can be written as,

$$D_{\text{global}} = R^T D_{\text{local}},$$

$$= R^T_\theta (R^T_\phi R^T_\psi D_{\text{local}}(\phi, \psi)) = R^T_\theta \tilde{D}(\phi, \psi),$$

$$S_{\text{global}} = R^T S_{\text{local}} R,$$

$$= R^T_\theta (R^T_\phi R^T_\psi S_{\text{local}}(\phi, \psi) R_\psi R_\phi) R_\theta = R^T_\theta \tilde{S}(\phi, \psi) R_\theta. \tag{3.25}$$

The expressions in (3.25) are then substituted into (3.19). Since the only dependence of $\theta$ in the integrand is $R_\theta$, which is completely known, integration over $\theta$ can be performed in advance. For any general $D_{\text{local}}(\phi, \psi)$ and $S_{\text{local}}(\phi, \psi)$ obtained from the crystallites, (3.19) can be reduced to

$$(D_{\text{ceramic}})_1 = (D_{\text{ceramic}})_2 = 0,$$

$$(D_{\text{ceramic}})_3 = \frac{1}{\pi} \int_0^\pi \int_0^{\frac{\pi}{2}} \tilde{D}_3(\phi, \psi) \sin \phi \psi d\phi d\psi,$$

$$(S_{\text{ceramic}})_1 = (S_{\text{ceramic}})_2 = \frac{1}{2\pi} \int_0^\pi \int_0^{\frac{\pi}{2}} (\tilde{S}_1(\phi, \psi) + \tilde{S}_2(\phi, \psi)) \sin \phi \psi d\phi d\psi,$$

$$(S_{\text{ceramic}})_3 = \frac{1}{\pi} \int_0^\pi \int_0^{\frac{\pi}{2}} \tilde{S}_3(\phi, \psi) \sin \phi \psi d\phi d\psi,$$

$$(S_{\text{ceramic}})_4 = (S_{\text{ceramic}})_5 = (S_{\text{ceramic}})_6 = 0. \tag{3.25}$$

For the series expansion method, the calculations of $N^p$ and $N^d$ using the integral in (3.21) remain unchanged. This is because the definitions of $N^p$ and $N^d$ are projections of the polarization components on the poling axis, which are inherently independent of $\theta$. However, the constitutive relations in (3.23) can be greatly simplified. In this thin plate model, the only variable of interest are $D_3$ and $S_1$. By specializing (3.23) into one-dimension, the following constitutive relations of the thin plate can be derived:

$$S = (s^l + s^N |N^l|) T + dN^l E - \mu|N^d|,$$

$$D = dN^l T + (\varepsilon^l + \varepsilon^N |N^l|) E + P_s N^l. \tag{3.26}$$

This series of simplifications has major effects in reducing required computations. First, since there is no dependence of $\theta$ in all the equations, only two Euler angles, $\phi$ and $\psi$, are needed to completely describe the whole group of crystallite orientations. Thus, if each of the Euler angle is discretized in $n$ points the total number of internal variables needed to represent all the crystallites in general will be $n^3$. In this case, the total number is reduced to $n^2$. This is a very significant reduction in terms of computation. Second, the structure of the total rotation matrix is also simplified, with $R_\theta$ becoming the identity matrix. This represents the second major reduction in computational effort due to the large
number of vector and tensor rotations required in the model. Third, (3.25) indicates that in general, there are only two distinct strain components and one electrical displacement component that are non-zero in the ceramic. Thus, only three integrations in (3.25) are required to determine the total responses of the ceramic instead of nine in the most general case. On the other hand, if the series expansion method is used, the implementation is much more straightforward. The axial symmetry still enables the model to be independent of $\theta$. After the states of polarization in the crystallites are completely determined, (3.21) and (3.26) can be directly used to compute the strain and electrical displacement in the ceramic.

3.5 SUMMARY

In this chapter, a model for ferroelectric ceramic was derived based on the multiple-family approach. Each family effectively represents crystallites in a ceramic body and behaves as piezoelectric crystals with an additional constant strain associated with a constant spontaneous polarization. Upon the application of a large external electric field and mechanical stresses, the spontaneous polarization can switch among six possible sites. Two sites are $180^\circ$ sites, which have no net strain associated with the polarization. The other four sites are $90^\circ$ sites, which will give some net strain positive strain in the direction parallel to the polarization. By considering the work done by the external loads in switching the polarization and the respective energy barriers associated with each site, switching of polarization can be determined through the principle of minimum potential energy.

After the behavior of a single crystal was established, a group of crystallites with random orientations was used to model the ceramic body. Each family is parameterized by a unique set of three Euler angles, which gives orientation of the crystallite with respect to the global reference frame of the ceramic. The external loads experienced by each crystallite are found by rotating the stress and electric field from the global frame into each of the crystal frames. In order to account for the physical variations among the crystallites in a real ceramic system, the energy barriers that control switching of polarization are modeled as a set of normally distributed random variables. With all of the above information and the single crystal model, the complete set of crystallite responses can be determined. Finally, two methods were devised to calculate the macroscopic strain and electrical displacement of the ceramic. The first method directly averages all the crystallite responses. The second method treats all of the macroscopic quantities as arbitrary functions of external loads as well as the internal alignment of crystallites. Series expansions of the macroscopic strain
and electrical displacement were then used to construct the one dimensional constitutive relations of the ceramic.

The general ceramic model can be simplified in many cases by exploiting the geometric symmetry of the actual ceramic. One such example concerning a thin plate with axial symmetric loading was derived. By using symmetry arguments, it was shown that tremendous simplifications in computation can be accomplished.
Chapter 4: Model Characterization and Simulation

In order to validate the multiple-family model derived in §3.4, simulations of clamped PZT wafers in sandwich structures using the model must be carried out. The model predictions can then be compared to the experimental data to reveal the strengths and the weaknesses of the model. The model behavior must first be characterized before any simulations can be done. There are two phases to the characterization process. The first phase is to determine the values of the model parameters. All the model parameters can be logically grouped into three groups. The first group directly affects the switching of polarization. The other two groups are associated with the two different methods derived to map the crystallite responses to the ceramic responses. Since most of the model parameters cannot be measured directly, their values were determined by matching physical constants derived from the hysteresis and butterfly loops of a stress-free PZT wafer with those given by the model. The detailed procedure used will be discussed in §4.1.

The second phase of the model characterization process is to understand the ways in which the model parameters influence the model behaviors. Several sets of simulations with different variations of model parameters were carried out for this investigation. Factors that were considered were the total number of families used in the simulations, the effects of back-switching parameter, $\gamma$, and the standard deviations of the distributions of the energy barriers, $U_p^{\text{rand}}$, $U_d^{\text{rand}}$, and $U_m^{\text{rand}}$.

Finally, there are still two unresolved issues that directly affect model implementation which are unique to the simulations of the sandwich structures. First, there is an additional constraint in these clamped cases that the applied stress on the ceramic is not an independent input. The stresses experienced by the ceramic are directly proportional to the resultant macroscopic strain, related by the extensional stiffnesses of the clamping elements. Thus, the value of stress is not available as a direct input to the model at any given time. Two methods were developed to estimate the stresses during the simulations, and they will be discussed in §4.2. The second issue is to choose a proper initial condition for the simulations so that the resultant ceramic will appear to be well-aged, to represent the actual ceramic used in the experiments. The results of these simulations were then compared to the experimental data, with further discussions on the performance.
4.1 MODEL CHARACTERIZATION

The parameters used in the model can be divided into three groups: parameters that are associated with switching, parameters that are associated with the nominal behavior of the crystallites used in the averaging method, and the parameters that are contained in the macroscopic constitutive relations of the series expansion method. Parameters that belong to the first group are the means and the standard deviations of the energy barriers, the back-switching parameter, $\gamma$, the spontaneous polarization, $P_s$, and the elongation ratio of the lattice, $c/a$. Parameters that belong to the second group are the linear piezoelectric constitutive properties of the crystallites. Parameters that belong to the third group are the coefficients appearing in the series expansions of the macroscopic strain and electrical displacement. The variables included in each group are summarized in Table 4-1. Since most of the model parameters are unavailable for direct measurements, the actual determination of most of the values were accomplished by matching the same properties of the hysteresis and butterfly loops of the model and experimental data. For example, piezoelectric constants observed in the butterfly loop at zero field were used to determine the model parameters that are associated with piezoelectricity. The actual matching of these physical quantities were done by using the bisection method on some initial guesses of the parameter values. The tolerance of the bisection method was set to 2% for all of the following characterization procedures.

<table>
<thead>
<tr>
<th>Switching Parameters</th>
<th>$P_s$, $c/a$, $\langle U_p \rangle$, $\langle U_d \rangle$, $\langle U_m \rangle$, $U_p^{rand}$, $U_d^{rand}$, $U_m^{rand}$, $\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite Properties</td>
<td>$s_{ij}$, $\epsilon_{ij}$, $d_{ij}$</td>
</tr>
<tr>
<td>Series Expansion Coefficients</td>
<td>$s^I$, $s^N$, $\epsilon^I$, $\epsilon^N$, $d$, $h$, $P_s$</td>
</tr>
</tbody>
</table>

While the first group mostly affects the global behavior of the model, the second and the third group mostly affect the local behavior of the model. It is impossible to directly quantify the sensitivity of model behavior to parameter variations due to the complex manner in which these parameters appear in the model. A set of nominal values for all the parameters will be chosen based on the free responses of the PZT wafers for both the direct averaging method and the series expansion method, respectively. The results from both methods will be compared and discussed. Methods and guidelines used in choosing the values will be discussed in §4.1.2, §4.1.3, and §4.1.4. The influence of different parameters on the model behavior will be discussed in §4.1.5.
4.1.1 Structure of Simulations

Since most of the characterization procedures require simulations of the model, the structure of the program that simulates the ceramic model must first be established. The most straightforward fashion to carry out the simulation is to directly employ the equations in §3.2 and §3.3. However, such a method is extremely inefficient. Many quantities such as the rotation matrices for stress and strain are independent of time and can be calculated before the simulation starts. Even other quantities that depend on the state of the polarization, such as the rotated material constants, can be calculated ahead of time since there are only six possible configurations and the values do not pose any storage problems. Many of these procedures were used in the actual simulations to minimize the required computational effort.

The program that was used to simulate the model was written in C. The complete source code is included in Appendix B. The model predictions were obtained by a simulation of a 1600-family model, with both $\phi$ and $\psi$ evenly discretized into 40 points in their respective ranges. The third Euler angle, $\theta$ is not needed in this case because both the geometry and the loading of the system are axially symmetric, as discussed in §3.4. The set of energy barriers for each run was generated by a random number generator before the simulation began. For a generic simulation, where stress and electric field are known functions of time, the structure of the program is given in the following flowchart. The actual steps will vary in cases where clamping stresses are present. Measures taken to augment this procedure will be discussed in §4.2. The typical run time of the program listed in Appendix B, with 1600 families and 400 time steps, on a IBM POWERStation 320 workstation is about two minutes.
4.1.2 Determination of Switching Parameters

There are altogether nine parameters in this group. Two of them, $P_z$ and $\mathcal{C}_a$, the spontaneous polarization in the lattice and the lattice ratio, are properties of the particular composition of the ceramic. Their values determine the amount of remanent polarization and strain, respectively, that appear in the ceramic. However, a reliable value of $P_z$ for PZT is not available. The closest estimate of $P_z$ for pure lead titanate is about 0.81 C/m$^2$ [64, p.118]. Thus, it is expected that PZT will also have similar amount of spontaneous polarization. The exact value of $P_z$ used in this model is 0.644 C/m$^2$, obtained by matching the remanent polarization of the model prediction and the actual dielectric responses of the PZT using the bisection method mentioned in the beginning of the section. The value of $\mathcal{C}_a$ for any composition of PZT can be determined more accurately. However, since the composition of PZT that displays ferroelectricity is very close to the tetragonal/rhombohedral phase boundary [64, p.137], slight variations introduced by impurities can dramatically alter the actual value. Nonetheless, the composition is assumed to be PZT 53/47 (with 47% PbTiO$_3$, by mole), and the $\mathcal{C}_a$ ratio for this composition is 1.022 [65].
The other seven parameters are the means and standard deviations of the energy barriers, and the back-switching parameter \( \gamma \). The value of \( \gamma \) determines the fraction of strain energy (stored in the neighbors caused by a 90° switching) that is available to help switch the spontaneous polarization back to a 0° or a 180° position. Since the effects of the value of \( \gamma \) on the material behavior is not clear, it is taken to be 1.0 for all the characterization processes. The investigation of its influences on model behaviors will be deferred to \S 4.1.4.

On the other hand, the role of the energy barriers are quite obvious in the physical sense. The ratios between \( P_s \) and the means \( \langle U_p \rangle \) and \( \langle U_d \rangle \) basically control the coercive field predicted by the model. This can be easily demonstrated by examining the qualitative behavior of switching of a single crystallite under stress free conditions. From (3.6), switching will occur when \( \Pi < 0 \). This translates to,

\[
U - E P_s < 0 \\
\Rightarrow E > \frac{U}{P_s}
\]

Thus, the ratio \( \frac{U}{P_s} \) basically is the value of the coercive field of the crystallite. Although the actual ceramic model contains a distribution of energy barriers, with both 180° and 90° switchings, and possibly with external stresses, \( \langle U_p \rangle \) and \( \langle U_d \rangle \) still carry the same significance. With the value of \( P_s \) already fixed, \( \langle U_p \rangle \) and \( \langle U_d \rangle \) can be determined by matching the coercive field observed in the hysteresis loop of a stress-free PZT wafer. The value of \( \langle U_m \rangle \) was set to be the difference between \( \langle U_p \rangle \) and \( \langle U_d \rangle \). This makes the coercive field of both 180° and 90° switchings to be the same, as observed in the hysteresis loop. The nominal values chosen for these parameters are summarized in Table 4-2.

Table 4-2. Nominal numerical values of switching parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_s ) (C/m²)</td>
<td>0.644</td>
</tr>
<tr>
<td>( c/a )</td>
<td>1.022</td>
</tr>
<tr>
<td>( \langle U_p \rangle ) (10⁴ J/m³)</td>
<td>77.30</td>
</tr>
<tr>
<td>( U_p^{rand} ) (10⁴ J/m³)</td>
<td>6.44</td>
</tr>
<tr>
<td>( \langle U_d \rangle ) (10⁴ J/m³)</td>
<td>64.4</td>
</tr>
<tr>
<td>( U_d^{rand} ) (10⁴ J/m³)</td>
<td>10.20</td>
</tr>
<tr>
<td>( \langle U_m \rangle ) (10⁴ J/m³)</td>
<td>12.90</td>
</tr>
<tr>
<td>( U_m^{rand} ) (10⁴ J/m³)</td>
<td>2.67</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>1.0</td>
</tr>
</tbody>
</table>
4.1.3 Determination of Crystallite Constitutive Properties

Since PZT is a two phase solid solution of lead zirconate and lead titanate, PZT crystals do not exist. Thus, it is necessary to obtain the constitutive properties of the crystallites from other sources. One possible way is to use the constitutive properties of barium titanate crystals and ceramics. Due to the similarities in the material structures of PZT and barium titanate, it can be argued that the ratio between the crystal and ceramic properties of barium titanate is also similar to that of PZT. Thus, by knowing the constitutive properties of barium titanate crystal and ceramic, and that of PZT ceramic, the constitutive properties of the crystallite in the model for PZT can be calculated. For instance, the dielectric permittivity of the crystallite along the polar axis (3-axis) can be obtained by,

\[(\varepsilon_{33})_{\text{PZT crystall}} = \frac{(\varepsilon_{33})_{\text{BT crystal}}}{(\varepsilon_{33})_{\text{BT ceramic}}} \cdot (\varepsilon_{33})_{\text{PZT ceramic}}.\]  (4.1)

By using PZT-5H material constants supplied by the manufacturer [65], and the material constants of barium titanate crystal and ceramic from Reference 64, the material constants for the crystallite were obtained by this method and are summarized in Table 4-3.

However, it is also recognized even though this extrapolation may seem reasonable, there is no physical ground to support this argument. Thus, instead of using the results of this extrapolation directly in the model, they were used as the initial guesses of the PZT crystallite constitutive properties for the bisection method, which directly fit the model behavior to the hysteresis and the butterfly loop. However, the disadvantage of this approach is that the final values of some of the material constants, most noticeably with the piezoelectric constants, are significantly varied from the expected range. This removes a certain amount of physical meaning from the material constants as the compliances of the crystallite. To retain some physical connections, the parameters were adjusted in three groups, the mechanical compliances, the dielectric permittivities, and the piezoelectric constants. Instead of adjusting all eleven constants independently and simultaneously, the ratios among the groups are adjusted independently.

For the dielectric permittivities of the crystallites, the extrapolated values were used to initialize the bisection method which scales both \(\varepsilon_{11}\) and \(\varepsilon_{33}\) by a single constant. The objective of the bisection search is to match the slope of the hysteresis loop at zero field in the experimental data and value given by the model. Similarly, all the piezoelectric coefficients were found by multiplying by a single constant to match the slope of the butterfly loop at zero field, which represents \(d_{31}\) of a completely polarized ceramic. The
procedure of finding the crystallite compliances is similar, except that a separate simulation of the model using zero field and a 2 MPa sinusoidal stress signal was run to determine the ceramic compliance predicted by the model to match the $s_{11}^E$ provided by the manufacturer.

The result of these kind of adjustments is that certain physical significance relevant to the structure of the material is preserved. The most obvious example is the ratio between the dielectric permittivities. In real barium titanate crystals, it is observed that $\varepsilon_{33}$ is much smaller than $\varepsilon_{11}$. The reason for this is that the titanate ion in the body center is displaced along the polar axis (3-axis) in the crystal lattice. As a result, it is closer to one of the faces perpendicular to the polar axis, and thus less mobile in that direction. Such a constraint does not exist in the other two axes and this effect manifests itself in the relative magnitude of the dielectric permittivities [64, p.72]. In ceramic barium titanate, such anisotropy is smeared out by the random orientations of the crystallites, and the permittivities in 1- and 3-directions are about the same. By adjusting all the dielectric parameters together, the anisotropy is preserved, as seen in Table 4-3, where the values of the material constant obtained by this method are summarized.

Comparison of experimental data from a stress-free PZT wafer and the results of the simulation based on this set of crystallite properties and the nominal switching parameters chosen in Table 4-2 are shown in Figure 4-2.

Table 4-3. Numerical values of the constitutive properties of PZT crystallites extrapolated from constitutive properties of barium titanate crystal and ceramic.

<table>
<thead>
<tr>
<th>Crystallite Properties</th>
<th>Extrapolated</th>
<th>Fitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_{11}$ ($10^{-12}$ $m^2/N$)</td>
<td>14.69</td>
<td>18.36</td>
</tr>
<tr>
<td>$s_{12}$ ($10^{-12}$ $m^2/N$)</td>
<td>-4.30</td>
<td>-5.38</td>
</tr>
<tr>
<td>$s_{13}$ ($10^{-12}$ $m^2/N$)</td>
<td>-15.54</td>
<td>-19.43</td>
</tr>
<tr>
<td>$s_{33}$ ($10^{-12}$ $m^2/N$)</td>
<td>36.39</td>
<td>45.49</td>
</tr>
<tr>
<td>$s_{44}$ ($10^{-12}$ $m^2/N$)</td>
<td>34.35</td>
<td>42.94</td>
</tr>
<tr>
<td>$s_{66}$ ($10^{-12}$ $m^2/N$)</td>
<td>16.50</td>
<td>20.62</td>
</tr>
<tr>
<td>$\varepsilon_{11}$ ($nF/m$)</td>
<td>50.00</td>
<td>143.80</td>
</tr>
<tr>
<td>$\varepsilon_{33}$ ($nF/m$)</td>
<td>2.66</td>
<td>7.648</td>
</tr>
<tr>
<td>$d_{31}$ ($10^{-10}$ $m/V$)</td>
<td>-1.088</td>
<td>-9.180</td>
</tr>
<tr>
<td>$d_{33}$ ($10^{-10}$ $m/V$)</td>
<td>2.658</td>
<td>22.430</td>
</tr>
<tr>
<td>$d_{15}$ ($10^{-10}$ $m/V$)</td>
<td>10.758</td>
<td>90.770</td>
</tr>
</tbody>
</table>
Figure 4-2. Comparison of experimental data of electrical displacement and strain (points) with simulation of model using the fitted material constants in Table 4-3 for the averaging method (solid line), and simulation with material constants in Table 4-4 for the series expansion method (dotted line).

4.1.4 Determination of Parameters in Series Expansion Method

Unlike the parameters in the crystallite constitutive relations, the parameters in the macroscopic constitutive relations obtained from the series expansions do relate to the actual ceramic properties. Thus, some of the results of low field characterization procedure in Chapter 2 can be used directly. Recall in (3.26),

\[
S = (s^I + s^N|N^I|)T + dN^I E - h|N^d|,
D = dN^I T + (\varepsilon^I + \varepsilon^N|N^I|)E + P_s N^I.
\]

Parameters appearing in the series expansions are the isotropic compliance of the unpoled ceramic, \(s^I\), the additional compliance due to poling, \(s^N\), their dielectric counterpart, \(\varepsilon^I\) and \(\varepsilon^N\), the electromechanical coupling \(d\), and finally quantities related to the remanent strain and polarization, \(h\) and \(P_s\). Among them \(P_s\), \(s^I\), and \(\varepsilon^I\) are already determined from various sources. \(P_s\) is determined to be 0.644 c/m² from §4.1.2. The compliance and the dielectric permittivity of the unpoled disks were measured in Chapter 2. However, the rest of the parameters cannot be determined directly from measurements with the poled samples. This is because the poled samples were properly aged during the
manufacturing process, and the material properties are significantly changed from those observed in the hysteresis loop. Therefore, the remaining material constants were determined by using a procedure similar to that used in the previous section, i.e., by matching the physical constants measured in the hysteresis and butterfly loops at zero field. Since the simulation with \( N_i \) and \( N_d \) only requires the switching parameters, they were done in advance to determine their values at zero field. Thus, by equating the material constants measured in the hysteresis and the butterfly loop with those appear in (3.26) the following relations can be derived.

\[
\begin{align*}
d_{31} &= d N_{t_0} \quad \Rightarrow \quad d = \frac{d_{31}}{N_{t_0}} \\
\varepsilon_{11}^{T} &= (\varepsilon' + \varepsilon^{N} N_{t_0}) \quad \Rightarrow \quad \varepsilon^{N} = \frac{(\varepsilon_{11}^{T} - \varepsilon')}{N_{t_0}} \\
S_{11}^{E} &= (s' + s^{N} N_{t_0}) \quad \Rightarrow \quad s^{N} = \frac{(s_{11}^{E} - s')}{N_{t_0}} \\
S_r &= h N_{d_0} \quad \Rightarrow \quad h = \frac{S_r}{N_{d_0}}.
\end{align*}
\]

(4.2)

\( N_{t_0} \) and \( N_{d_0} \) are the positive values of \( N_i \) and \( N_d \) of a fully polarized ceramic under no external loads. The quantities \( d_{31} \) and \( \varepsilon_{11}^{T} \) were directly measured from the butterfly and the hysteresis loops, respectively. The compliance \( S_{11}^{E} \) was obtained from the resonant tests done in Chapter 2. \( S_r \) is the remanent strain of the ceramic measured from the virgin state of the material. Since there is no data of \( S_r \) available, its value was estimated by using the averaging method derived in the previous section. The final values of all the parameters are summarized in Table 4-4. The result of the model simulation based on the series expansion method with parameters in Table 4-4 is also shown in Figure 4-2.
Table 4-4. Numerical values of the constitutive properties appearing in the series expansion.

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Fitted Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>0.4632</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.1315</td>
</tr>
<tr>
<td>$s^I(10^{-12} m^2/N)$</td>
<td>13.93</td>
</tr>
<tr>
<td>$s^N(10^{-12} m^2/N)$</td>
<td>3.60</td>
</tr>
<tr>
<td>$\varepsilon^I(nF/m)$</td>
<td>19.14</td>
</tr>
<tr>
<td>$\varepsilon^N(nF/m)$</td>
<td>155.30</td>
</tr>
<tr>
<td>$d(10^{-10} m/V)$</td>
<td>-16.00</td>
</tr>
<tr>
<td>$h$</td>
<td>5.3x10^{-3}</td>
</tr>
<tr>
<td>$P_s(C/m^2)$</td>
<td>0.644</td>
</tr>
</tbody>
</table>

From this point on, all values of the model parameters given in Table 4-2, Table 4-3 and Table 4-4 will be the nominal values, and will be used to produce all the model predictions unless otherwise stated. It is interesting to note that the both methods of calculating strain overpredict the peak strain level due to the lack of saturation mechanism in the model. However, this does not present a serious problem since adding in saturation terms in the model formulation is quite straightforward. Finally, it is important to point out that all the model characterization were done with stress-free data. Thus, the major challenge for the model is to use these information extracted from the stress-free data to predict results in the clamped cases.

4.1.5 Investigations of Model Size and Switching Parameter Variations

After the set of nominal values for the all the model parameters are determined, the effects of parameter variations on model behaviors can be studied. In this section, only the effects of variations on the switching parameters are studied; the impact of variations on material constants of crystallites were quite well illustrated in the previous section. Due to the large number of parameters, a thorough and rigorous study that covers all the possible variations is not possible. Fortunately, the effects of $P_s$, $\gamma_a$, and the means of the energy barriers are already quite apparent from the discussions in §4.1.2. The only remaining parameters are the back-switching factor $\gamma$, and the standard deviations of the energy barrier distribution. One other possible variation is the size of the model, i.e., the total number of families used in the simulations. Thus, the variations on the parameters will be done in three group
starting with the nominal values. The first group is on the number of families, the second on \( \gamma \), and the final group on the standard deviations of the energy barriers.

The first series is the variation on the number of families used in the simulation. In this series of simulations, a single run of models with different numbers of families will be compared. The values for all the model parameters used in these simulations are the nominal values. The discretization of the Euler angles are summarized in Table 4-5. The results of the simulations are illustrated in Figure 4-3 and Figure 4-4. As expected, the number of families used in the simulation directly influences the smoothness of the output from the model. In all cases, the model behavior is well captured except for the ceramic strain when the system is close to polarization reversal. The model responses given by both methods are very similar. One exception is that the series expansion method consistently produces a longer and sharper tails in the butterfly loops during polarization reversal. For all practical purposes, results given by models with more than 1600 families are almost exactly the same.

Table 4-5. Total number of families used and the discretization of the Euler angles

<table>
<thead>
<tr>
<th>Number of points in ( \phi ) ((0,\pi))</th>
<th>Number of points in ( \psi ) ((0, \frac{\pi}{2}))</th>
<th>Total number of families</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>20</td>
<td>400</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>900</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>1600</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
<td>3600</td>
</tr>
<tr>
<td>70</td>
<td>70</td>
<td>4900</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>10000</td>
</tr>
</tbody>
</table>

The second series of simulations were carried out with varying values of \( \gamma \). The nominal value of \( \gamma \) is 1.0, which means that all the strain energy stored due to a 90° switching of a crystallite is available to help overcome the energy barrier when switching back to a 180° site. Since the maximum value of \( \gamma \) is 1.0, three other simulations with \( \gamma \) equal to 0.0, 0.333, and 0.667 were run. The results of all four simulations are from a single run of the same 1600–family model described in §4.1.1, except with the value of \( \gamma \). The results are illustrated in Figure 4-5. There are three visible effects in decreasing \( \gamma \). First, the hysteresis loop becomes slightly more square. The tails in butterfly loops where reversal occurs in the strain from the series expansion method also become much sharper. Second, the inner edges of the butterfly loop straightened considerably near switching. Except in strains calculated by the series expansion method, where a sharp bend appears as
\( \gamma \) is decreased. Third, the amount of remanent strain increases in both the strain responses. All three observations are related to the fact that as back-switching is discouraged (decreasing \( \gamma \)), more of the crystallites stay in 90° sites longer, thus accounting for the increase of remanent strain. The lack of back-switching also means that crystallites more likely to stay in their present configuration for a longer period of time, since the amount of energy available for them to switch out is less. Thus, switching will occur altogether more abruptly instead of happening over a wider range of field level, which explains the first two observations. As to the sharper and longer tails of the butterfly loops from the series expansion method, it can be attributed to the absolute sign in the constitutive equation of strain in (3.23). During reversal, \( N_d \) changes sign rather abruptly, just as observed in the hysteresis loop of the electrical displacement. The absolute value of \( N_d \) in the strain equation forces that term to vanish when \( N_d \) goes across the axis. If the rate at which \( N_d \) changes sign is large, the resultant strain response calculated from (3.23) will have a sharp corner. As \( \gamma \) approaches 1.0, the switching of the crystallites tend to spread out over a larger range of field. As a result, the slope of \( N_d \) when crossing the axis is much gentler, resulting in smoother tails in the butterfly loop.

The third set of simulations were carried out on the same 1600-family models with varying standard deviations in the distributions of energy barriers. This is accomplished by varying all the standard deviations with fixed percentages of the nominal values. Three cases, with 50%, 100% and 150% of the nominal values of \( U_{p}^{\text{rand}} \), \( U_{d}^{\text{rand}} \), and \( U_{m}^{\text{rand}} \) were done. The results are illustrated in Figure 4-6. The most obvious differences among the simulations are in the shape of the hysteresis loops. As the standard deviations increase in size (energy barriers among crystallites become more widely distributed), the corners of the hysteresis loop become more and more smoothed. The smoothing effect is due to the fact that switching occurs under a much wider range of electric fields when the crystallites have very different values of energy barriers. For the series expansion method, another effect of the smoother reversal is that the value of \( N_t \) remains larger for a longer period of time when the model is very close to reversal. As a result, the piezoelectric term in (3.23) increases in magnitude in that region. Thus, the amount of strain produced also increases, creating longer tails in the butterfly as the standard deviations increase.
Figure 4-3. Hysteresis loops and butterfly loops from simulation of models with 400, 900, and 1600 families. The solid lines are calculated using the averaging method, and the dotted lines are calculated using the series expansion method.
Figure 4-4. Hysteresis loops and butterfly loops from simulation of models with 3600, 4900 and 10000 families. The solid lines are calculated using the averaging method, and the dotted lines are calculated using the series expansion method.
Figure 4.5. Hysteresis loops and butterfly loops from simulations of models with $\gamma$ equals to 0.0, 0.333, 0.666, and 1.0. The solid lines are calculated using the averaging method, and the dotted lines are calculated using the series expansion method.
Figure 4-6. Hysteresis loops and butterfly loops from simulation of models with 50%, 100% and 150% of the nominal values of $U_p^{\text{rand}}$, $U_d^{\text{rand}}$, and $U_m^{\text{rand}}$. The solid lines are calculated using the averaging method, and the dotted lines are calculated using the series expansion method.

In summary, the effects of these model parameters on the model behavior are as follows:
Increase total number of families
  • Smoother model responses, better approximations to the ceramic responses
Increase $\gamma$
  • Encourages back-switching from 90° sites
  • More nonlinear strain-field relation before polarization reversal
  • Increase in remanent strain
  • Sharper tails in the butterfly loops from the series expansion method
Increase standard deviations
  • Encourages switching of families over a wider range of field level.
  • Increase strain production near reversal for the series expansion method

One final note about this investigation is that all the comparisons are based on the set of nominal parameter values, which are themselves based on fitting of stress-free data. Thus, it is to be expected while the observed effects of these parameter variations are qualitatively valid, they are by no means generally true. As variations of two or more parameters occur simultaneously, it is not certain if any coupling of effects will happen, and the interaction can be complicated. Therefore, these results can only contribute to the understanding of some simple behaviors of the model, and thus may not be representative of the global qualitative behavior.

4.2 Simulations with Clamping Stress

In order to verify the validity of the model for cases where both large field and stresses are present, simulations must be carried out for situations that represent the sandwich structures tested in Chapter 2. In these cases where the stresses applied on the ceramic are induced by the host structure, the actual values of the stresses are directly proportional to the resultant strains. The simple dependence of stress on macroscopic strain can be demonstrated by considering a typical section of a perfectly bonded sandwich structure. The equilibrium condition on a typical section in Figure 4-7 is then

$$T_p t_p = -2T_s t_s.$$  

Since the bonding layers are assumed to be perfect, the strain in the structure is the same as the strain in the ceramic. Furthermore, by using the constitutive relation of the structure, the stress on the ceramic is then
\[ T_p = -\frac{2c_s t_s}{t_p} S_p \] (4.3)

Figure 4-7. Equilibrium of a typical section of a perfectly bonded sandwich structure.

Under these circumstances, the value of stress as a function of time, which was taken as a direct input to the model to determine the ceramic responses, is no longer available before the simulation starts. Since the macroscopic strain of the ceramic depends on the microscopic strains of all the families\(^1\), it is also impossible to express the resultant stress as an explicit function of the microscopic strains. Thus, an additional mechanism to estimate the resultant stress during the simulation must be used.

There are two possible approaches in solving this dilemma. The first approach is to simply use the value of the strain calculated from the previous time step to estimate the resultant stress using (4.3). It can be argued that if the time step is small enough as compared to the variation of the electric field, this method should provide a reasonable solution. The second approach is to directly impose (4.3) as a constraint in the calculation of the macroscopic strain. This method however, requires an iterative solution procedure. Both of these approaches will be fully investigated. Furthermore, it can be analytically shown that the first approach only converges in some special cases. In general, its solution will diverge. Since the second method directly imposes equilibrium, its solution will be guaranteed convergence, provided that the iterative method used to find the solution also guarantees convergence.

\(^1\) The relation between the microscopic and macroscopic quantities is not one-to-one, \textit{i.e.}, many different microscopic crystallite configurations can result in the same macroscopic strain or electrical displacement, since the macroscopic quantities simply represent the average behavior of the crystallites. This lack of uniqueness is precisely the reason that Taylor expansions of thermodynamic potentials cannot be rigorously applied to ceramic systems.
4.2.1 Previous Time Step Method

It is fairly straightforward to demonstrate analytically that this method will lead to divergence unless some special criterion is satisfied. The logic of this method is illustrated in the flowchart in Figure 4-8. To illustrate the basic flaw of this method, only an examination of a special loading case is needed. Consider a simple piezoelectric ceramic that obeys the linear constitutive relations, in which both the stiffness and the piezoelectric strain constant of the ceramic, \( c_p^E \) and \( d \), are known exactly and the applied field is constant. Thus the strain of the ceramic is,

\[
S = c_p^{E^{-1}} T + dE. \tag{4.4}
\]

From (2.15), the exact resultant strain in this case is \( \frac{dE}{1 + \psi} \), where \( \psi = \frac{2c_p t_s}{c_p^E T} \). Assume that this equilibrium configuration is not known and the previous time step method is used to estimate the stress. It is desirable for this solution to converge to the exact resultant strain.

To initialize the procedure, the strain in the zeroth time step is assumed to be some \( S_o \). The exact value of \( S_o \) is not important. Then, the stress for the next time step is calculated based on \( S_o \) and (4.3). Thus the resultant strain for the first time step is,

\[
S_1 = (dE - S_o) + (1 - \psi)S_o. \tag{4.5}
\]

Similarly, the strains in the following time steps are,

\[
S_2 = (1 - \psi)(dE - S_o) + (1 - \psi + \psi^2)S_o,
\]

\[
S_3 = (1 - \psi + \psi^2)(dE - S_o) + (1 - \psi + \psi^2 - \psi^3)S_o,
\]

\[
S_4 = (1 - \psi + \psi^2 - \psi^3)(dE - S_o) + (1 - \psi + \psi^2 - \psi^3 + \psi^4)S_o,
\]

\[
S_n = \frac{1 - \psi^{n-1}}{1 - \psi} (dE - S_o) + \frac{1 - \psi^n}{1 - \psi} S_o. \tag{4.6}
\]

The strain at the \( n \)th time step calculated by this method is basically the sum of two geometric series. It can be easily seen that as \( n \) approaches infinity, the value of the relative stiffness, \( \psi \), becomes extremely important. If \( \psi < 1 \), the solution will converge to the correct resultant strain, \( \frac{dE}{1 + \psi} \), regardless of the value of \( S_o \). However, if \( \psi \geq 1 \), the solution will become unbounded. For cases where the material properties of the ceramic are not known explicitly, and the applied field does not remain constant, such a derivation becomes extremely complicated and the asymptotic behavior of the solution is not as apparent. Nonetheless, the examination of such a simple case reveals the essence of this method. The fundamental flaw in the logic of this method is that the equilibrium condition is never satisfied since an incorrect stress is used in the calculation in each time step,
regardless of the step size. The solution given by this method generally oscillates about the exact solution. If \( \psi < 1 \), the oscillation will eventually approach the exact solution. However, if \( \psi \geq 1 \), the magnitude of the oscillation will increase geometrically with time. Thus, when \( \psi < 1 \), this method can be expected to give a reasonable solution. However, when this condition is violated, it will be necessary to directly impose the equilibrium relation as a constraint when calculating the macroscopic strain.

![Flowchart](image)

Figure 4-8. The flowchart for the Previous Time Step Method for estimating clamping stresses in the sandwich structures.

### 4.2.2 Equilibrium Constraint Method

Since a closed form solution for the macroscopic strain is not available, the equilibrium condition cannot be directly imposed in the calculation. One way to circumvent this problem is to add another set of iterations in each time step: first assume a value for the resultant stress, solve for the macroscopic strain and then check to see if the equilibrium condition is approximately satisfied. If the iterative procedure used guarantees convergence, then the system is approximately in equilibrium in each time step.

Assuming that the macroscopic strain of the ceramic, \( S_p \), is a one-to-one, continuous, and monotonic function of the applied stress \( T_p \), under a constant electric field\(^2\), the equilibrium condition from (4.3) can be used to construct an indicator \( g(t, T_p) \),

\(^2\) It is not possible to verify this assumption due to the complexity of the model. From a physical point of view, this is certainly true for any elastic material. However, this assumption is most likely false when the ceramic is very close to a macroscopic polarization reversal. In those cases, a small change in stress can induce a large change in strain. This will correspond to the cases where \( g(T_p) \) has multiple closely spaced roots. Finding the "correct" root could be impossible.
\[ g(t, T_p) = S_p(T_p, E(t)) + \frac{t_p}{2c_s t_s} T_p. \] (4.7)

When the equilibrium condition is \textit{exactly} satisfied at an electric field \( E(t) \), then \( g(t, T_p) = 0 \). Thus, imposing the equilibrium condition in each time step basically becomes solving for the roots of \( g(t, T_p) = 0 \) at a constant field. The only remaining problems are to bracket the root in each time step and to find a sufficiently fast root searching algorithm.

Regardless of the choice of algorithm, the root of \( g(t, T_p) = 0 \) must first be bracketed. This involves finding a continuous region in \( T_p \) which contains the root of \( g(t, T_p) \). The only criterion for choosing the region is that the values of \( g(t, T_p) \) at the two boundary points of the region must have opposite signs. The procedure used in choosing the boundary points at each time step is as follows. Assuming that the equilibrium condition can be reach in the previous time step \( t_i \), with the electric field and equilibrium stress \( E(t_i) \) and \( T_p(t_i) \), respectively. At time step \( t_{i+1} \), the electric field is change to \( E(t_{i+1}) = E(t_i) + \Delta E \). Thus, the stress and strain in the ceramic will change to obey the equilibrium condition. Equation 4.7 can then be written as,

\[ g(t_{i+1}, T_p(t_i) + \Delta T) = S_p(T_p(t_i) + \Delta T, E(t_{i+1})) + \frac{t_p}{2c_s t_s} (T_p(t_i) + \Delta T). \] (4.8)

This equation will be used to choose the boundary points that start the iterations. The first boundary point is chosen by setting \( \Delta T = 0 \), \textit{i.e.}, the stress does not change between the two time steps. By exploiting the fact that \( g(t_i, T_p(t_i)) = 0 \), (4.8) can be reduced to,

\[ g(t_{i+1}, T_p(t_i)) = S_p(T_p(t_i), E(t_{i+1})) - S_p(T_p(t_i), E(t_i)), \]

\[ = \Delta S. \] (4.9)

This represents the change in strain in the ceramic due to the change of electric field at a constant stress level (the equilibrium stress in the previous time step). The second boundary point is chosen by setting \( \Delta T = -\frac{2c_s t_s}{t_p} \Delta S \). This corresponds to the additional stress needed to clamp the ceramic back to the strain level in the previous time step. Thus, (4.8) becomes,

\[ g(t_{i+1}, T_p(t_i) + \Delta T) = S_p(T_p(t_i) + \Delta T, E(t_{i+1})) + \frac{t_p}{2c_s t_s} T_p(t_i) - \Delta S. \] (4.10)

By using the definition of \( \Delta S \) in (4.9) and the equilibrium condition in (4.7), (4.10) is then reduced to,

\[ g(t_{i+1}, T_p(t_i) + \Delta T) = S_p(T_p(t_i) + \Delta T, E(t_{i+1})) - S_p(T_p(t_i), E(t_{i+1})), \] (4.11)

This represents the change in strain in the ceramic due to the change of stress at a constant electric field level (the electric field in the new time step).
The region in which the root search algorithm begins is then \([T_p(t_i), T_p(t_f) - \frac{2c_t}{t_p} \Delta S]\). There are several common algorithms available, such as the bisection method and the secant method. While different methods have very different approaches to the problem, their common goal is to decrease the size of the root bracket to a satisfactory accuracy through each step of iteration. There are several requirements for the root searching algorithm in this application. First, the algorithm must guarantee convergence. The bisection method satisfies this requirement. One way to guarantee convergence is to ensure that the estimate of the root in each step stays within the initial bracket, \(i.e.,\) the limits used in \(g(t, T_p)\). Furthermore, the derivative of \(g(t, T_p)\) is also not available, since an analytical expression of \(g(t, T_p)\) cannot be formed. These two restrictions basically imply that both the secant method and the Newton–Raphson method are not applicable. Aside from the issue of convergence, it is also desirable for the algorithm to be simple and have a fast rate of convergence. In terms of rate of convergence, the bisection method is the slowest; it converges linearly [67]. This means that the size of the interval that contains the root is decreased linearly with the size of the interval from the previous step; in this case, it is exactly halved. An alternate algorithm, the Ridder’s method is a superlinear algorithm that satisfies all the above requirements. It converges quadratically [67]. Each additional step of iteration doubles the number of significant figures in the root estimate. However, since it requires two function evaluations per iteration step (instead of one evaluation for bisection method), the effective rate of convergence is slightly lower than quadratic. Nonetheless, this method was chosen for this set of simulations. It should be noted that if there is more than one root present within the initial bracket, any one of these algorithms will converge only to one of them. This can prove to be troublesome when there are closely spaced roots in \(g(t, T_p)\).

With this augmentation to the simulation, the structure of the main loop of the program that simulates a sandwich structure, with electric field as the only known input to the model, is illustrated in the following flowchart. The number of iterations on the equilibrium condition needed (iterations within Ridder’s Method) depends on the desired precision. In general, about four iterations are needed if a tolerance of 10 Pa is required. It is important to note that unlike simulations with known stress and field, a separate simulation loop is needed for each method of calculating the ceramic responses. This is because the different methods in calculating the ceramic strain will result in different equilibrium stress induced in the ceramic. This will cause the internal states to be different in either cases. Thus, for a complete simulation of the sandwich structure, there will be two distinct sets of stress, strain, electrical displacement and internal states of the crystallites. The logic of this method is illustrated in the flowchart in Figure 4-9.
4.2.3 Model Initialization

In the case when simulations are done for sandwich structures, care must be taken to ensure the correct initial conditions are applied. Before any procedure to initialize the model, all the crystallites are in their reference state. Thus, the model represents a ceramic in the virgin state, with no remanent polarization or remanent strain. However, in the ceramics bonded inside the structure, proper poling and aging procedures were already applied during the manufacturing process. Thus, the model must be initialized in such a way so that the states of the crystallites reflect the states of a properly poled ceramic. Usually, PZT–5H ceramics are poled with a constant field of about 1600 V/mm. However, the ceramic typically has substantially higher piezoelectric constants as well as dielectric permittivity immediately after poling, which decay with respect to time. Therefore, poled specimens have to undergo an aging period, so that all the material constants settle to
steady state values. It proved to be difficult to reproduce such procedures in initializing the model. While the model can be initialized at a high field under stress-free conditions to obtain some initial piezoelectricity, the piezoelectric constants in these cases will be much higher than the manufacturer's figures. Since there is no aging mechanism present in the model, the piezoelectric constants and the dielectric permittivity will not decay to steady state values, as in real ceramics. One way to cope with this difficulty is to initialize the model with an *effective poling field*, such that the piezoelectric constants exhibit by the model after poling will match the steady state values. Since the ceramics in this case operate exclusively in the planar mode, $d_{31}$ was chosen to be matched. By using the bisection method identical to that used in the characterization procedure, it was found that an effective poling field of 893.8 V/mm will approximately initialize the model to a state with $d_{31}$ within 2% of $-2.49 \times 10^{-10}$ m/V. Thus, all the following simulations used this effective poling field level to initialize the model.

Another important initial condition is the initial strain of the ceramic. After the above initialization procedure, the model will have a remanent strain. This is because strain is measured with respect to the virgin state of the model. However, in the real ceramic wafers used in the sandwich structures, the zero strain state is the state after the ceramic is polarized, *i.e.*, the real ceramic has zero strain when there is some piezoelectricity in the ceramic. For simulations on stress-free ceramics, this does not present any serious problem. This only means that the strain output of the model has a d.c. offset from the strain gage measurements, which is equal to the remanent strain created by the poling procedure. However, the situation is completely different in the simulations for the sandwich structures. In these cases, the macroscopic strain of the structure is related to the induced stress in the ceramic. Therefore, the amount of remanent strain due to poling must be subtracted from the strain output of the model to yield the correct strain level.

**4.3 COMPARISON WITH EXPERIMENTAL RESULTS**

Simulations of the sandwich structures were carried out for all the field levels and relative stiffnesses contained in Table 2-4. The evaluation of the model is done in both a qualitative and a quantitative fashion. There are two variables involved in the experiments, the applied field level and the degree of clamping, represented by the relative stiffness of the sandwich structures, $\psi$. Three series of qualitative comparisons between the model and data of different clamping and applied field will be carried out. These comparisons will identify the
region in the test matrix which the model gives the best performance for the two different methods of calculating the ceramic responses.

In the quantitative comparisons, specific features of the hysteresis and butterfly loops are compared. The list of comparisons includes the coercive field, the remanent polarization, $d_{31}$, $e_{11}$ and the peak-to-peak strain. Finally, the high field stress–strain map of PZT–5H is constructed for different field level to illustrate the nonlinearity in the material. This series of studies will establish an index to measure the performance of the model and to derive numerical figures that can be useful in the utilization of PZT–5H in actual high field applications.

4.3.1 Qualitative Comparisons

There are three series of comparison shown in this section. The first is the progression of polarization reversal in a stress-free sample as applied field was increased. The second is the progression of polarization reversal in a slightly clamped sandwich. The third is the fully formed hysteresis and butterfly loops at different clamping.

a. Polarization Reversal in Stress-Free Ceramic

The first series of comparisons on the behavior of the ceramic and the model under stress-free conditions at various peak field levels are illustrated in Figure 4-10 and Figure 4-11. The six peak field levels displayed range from low levels, where no polarization reversal has taken place, through high levels, where complete polarization reversal is achieved every cycle. The behavior of the model in the transition into full polarization reversal is not entirely the same as the real ceramic. There are several omission of physical effects in the model. The most visible one in the lower field loops is the absence of hysteresis not associated with large scale polarization reversal. The low field hysteresis is really caused by domain walls movement within the crystallites. In soft PZTs such as PZT–5H, where dopants are used to increase the domain wall mobility, this effect is particularly noticeable. However, since the crystallites are modeled as single domain crystals, domain wall movement is entirely ignored. Thus, it is not surprising that there is no low field hysteresis appearing in both the strain and electrical displacement ($E_{max}=472.4$ V/mm and 629.9 V/mm). However, the mismatch of the remanent polarization levels in the low peak field cases are not caused by the model. In the real ceramics used in the experiments were in short circuit conditions in the beginning. Thus, surface charges in the ceramics were set up to compensate the remanent polarization creates by poling. It can be seen that as the field
level was increased, the effect of the surface charges gradually disappear and the model agrees with the data in the remanent polarization. A another omission is a saturation mechanism in the model. This is manifested in the butterfly loops at high field. The field–strain relation of real ceramics tend to deviate from the linear prediction when the high field is in the poling direction. In that region, the strain produced in the ceramic starts to saturate, which is not predicted by the model. This deficiency leads to a fairly linear field–strain relation in the model when the field is in the poling direction ($E_{\text{max}}=944.9$ V/mm). The reason for this omission is that the crystallites are assumed to be perfectly piezoelectric when the field is parallel to the polar axis. Finally, the rate at which the ceramic progresses into full polarization reversal is much faster than that predicted by the model. The experimental data show that reversal does not occur until $E_{\text{max}}$ reaches 708.4 V/mm, which is accompanied by the sudden appearing of a second loop in the field–strain relation and the sudden enlargement of the hysteresis loop of the electrical displacement. The full hysteresis and butterfly loops are almost completely formed when $E_{\text{max}}$ reaches 787.4 V/mm. The remanent polarization and the peak-to-peak strain change very little as $E_{\text{max}}$ is increased further. However, the model predicts that reversal starts much earlier ($E_{\text{max}}=629.9$ V/mm) and gradually arrives at the complete reversal as $E_{\text{max}}$ is increased. The value of the remanent polarization in the model does not catch up with the remanent polarization in the data until $E_{\text{max}}$ reaches 944.9 V/mm.

Aside from these omissions, the model does capture many of the essential features of the reversal in the ceramic. Both methods of calculating the ceramic responses perform very similarly. This is partly because the model parameters involved in both methods were characterized using very similar procedures with the same set of experimental data. Similarly, the slope of the field–strain relation at $E_{\text{max}}=427.4$ V/mm matches almost exactly, which is a direct result of the method used to choose the effective poling field. The agreement between model data is not so well at the intermediate field levels. However, the agreement in the shape and size of the hysteresis loop in full reversal is quite remarkable ($E_{\text{max}}=944.9$ V/mm). The agreement in the strain prediction is not as satisfactory as that of the electrical displacement. One of the discrepancies is that the two sides of the butterfly are not of the same shape. This can be attributed to the poling procedure used to initialize the model. While all the effects from poling completely disappeared from the real ceramics, the model does preserve some residual effects, probably due to the lack of an aging mechanism. In general, the model prediction does contain most of the essential details of the material behaviors. One area that is of particular importance is the at the upper tips of the butterfly, where the ceramic is close to a full polarization reversal. The shapes of the
loop in those areas are well predicted by the model. This is a good indication that process of polarization reversal at the crystallite level is indeed well-modeled.
Figure 4-10. Comparison of experimental data from stress-free PZT–5H with the model predictions from the two different methods in calculating the ceramic responses at different peak field levels before full polarization reversal. The points are the actual experimental data, the solid lines are the model predictions based on the averaging method, and the dotted line are predictions based on the series expansion method.
Figure 4-11. Comparison of experimental data from stress-free PZT-5H with the model predictions from the two different methods in calculating the ceramic responses at different peak field levels approaching full polarization reversal. The points are the actual experimental data, the solid lines are the model predictions based on the averaging method, and the dotted line are predictions based on the series expansion method.
b. Polarization Reversal in Lightly Clamped Ceramic

The second series of comparison is the sequence of responses of the ceramic and the model under lightly clamped situation. In this sequence, the sandwich structures has $\varphi=0.61$. The results of this comparison is shown in Figure 4-12 and Figure 4-13. This will illustrate the differences in the transition into full reversal introduced by clamping. Although the amount of clamping in these sandwiches are quite mild, there are some definite changes in model behaviors. The behavior of the actual data does not change very much, except for the peak strain which is reduced by the clamping. In the model predictions of the electrical displacement, the most visible changes are mismatch of slopes of the hysteresis loops and the difference in the remanent polarization. Even in low field region, the dielectric permittivity (slope of the loop at zero field) predicted by the two method are quite different. The averaging method predicts a higher permittivity, with the prediction from the series expansion method closer to the actual value. This difference occurs throughout the whole range of applied field. When full reversal is achieved, another noticeable difference is the amount of remanent polarization predicted by the model. Both methods predicts similar amount of remanent polarization in the ceramic, which is significantly lower than the actual value. A more detailed comparison of these discrepancies will be discussed in §4.3.2.

The quality of strain prediction by the model does not improve in this case. As a matter of fact, the strain prediction degraded slightly near the reversal. This is due to the numerical problems introduced in the algorithm used to determined the stress within the ceramic discussed in §4.2.2. However, the degradation is not too severe in this case and the overall strain prediction at full reversal is still better than that of the actuation strain assumption. It is interesting to note that as the applied field is increased to 629.9 V/mm, where partial reversal starts in the model, the two different methods behave quite differently. For the averaging method, the second loop in the strain prediction starts at the lower end of the loop. However, the series expansion method predicts that the second loop starts at the upper end of the loop, which agrees with the actual behavior of the ceramic. It is not certain how such discrepancy arises. Closer examination of the model behavior will be needed to clarify such contradiction.
$E_{\text{max}} = 472.4 \text{ V/mm}$

$E_{\text{max}} = 629.9 \text{ V/mm}$

$E_{\text{max}} = 708.4 \text{ V/mm}$

Figure 4-12. Comparison of experimental data from sandwich structures with $\psi=0.61$ with the model predictions from the two different methods in calculating the ceramic responses at different peak field levels before full polarization reversal. The points are the actual experimental data, the solid lines are the model predictions based on the averaging method, and the dotted line are predictions based on the series expansion method.
$E_{\text{max}} = 787.4 \text{ V/mm}$

$E_{\text{max}} = 866.1 \text{ V/mm}$

$E_{\text{max}} = 944.9 \text{ V/mm}$

Figure 4-13. Comparison of experimental data from sandwich structures with $\psi = 0.61$ with the model predictions from the two different methods in calculating the ceramic responses at different peak field levels before full polarization reversal. The points are the actual experimental data, the solid lines are the model predictions based on the averaging method, and the dotted line are predictions based on the series expansion method.
c. Effect of Clamping on Full Polarization Reversal

The series of fully developed hysteresis and butterfly loops under various clamping conditions are shown in Figure 4-14 and Figure 4-15. In these cases where the PZT is constrained in the sandwich structures, one effect unrelated to material modeling surfaced. As the relative stiffness increases (increase in induced stress), the model predictions become noticeably more jagged. This is exactly the result of multiple closely spaced equilibrium points discussed in §4.2.2. Since the root searching algorithm used to find the equilibrium stress level can only find one of the roots, the result is a very jagged output, as the model jumps to a different equilibrium point in each time step. Closer examination on the strain output indicates that such a problem occurs only when the model is close to, or in the process of polarization reversal. Otherwise, the strain prediction is still quite smooth. Since polarization reversal is a rather catastrophic effect, this observation is to be expected. Any small change in the input variable (stress in this case) will result in a drastically different output. This problem worsens progressively as \( \psi \) increases. At the highest clamping cases, large spikes show up and corrupt the strain predictions. One possible way to circumvent such problem is to use a least square fit of a polynomial to interpolate the noisy part of the prediction. Although this is an ad hoc method, a reasonable amount of information can still be extracted from the model predictions since the trend of the prediction follows the data quite well. It is interesting to note that clamping does not noticeably affect the quality of the electrical displacement predictions similar to the ways the strain predictions are affected.

Another problem associated with the model is the sensitivity of the series expansion method to the degree of clamping. For all the cases with \( \psi \) greater than 0.61, the series expansion method produces no reasonable predictions. Upon closer examination of the model, it was revealed that the cause for such problem was fundamental to the way the ceramic responses are calculated from the crystallite responses. In the series expansion method, both the tensorial and the vectorial nature of strain and electrical displacement were neglected for simplicity. Instead, an effective alignment represented by \( N_t \) and \( N_d \) was used. However, these two variables are merely the projections of the of net alignment of the crystallite polarization on the polar axis of the ceramic. In clamped cases, their values are extremely sensitive to the value of the equilibrium stress. Switching of some crystallites introduce large changes in the values of these variable. As a result, as the degree of clamping increases, the history of the equilibrium stress is no longer smooth, the predictions degrade to point where no significant information can be extracted. Thus, the
series expansion method is abandoned in the cases where $\psi$ is greater than 0.61. This represents a major limitation in the series expansion method.

Problems such as lack of saturation and discrepancy in the remanent polarization observed in the previous comparisons also show up. However, aside from the artifacts of the simulation algorithm and the problem with the series expansion method, the model does a much better job in estimating the induced strain level than the actuation strain assumption, especially in high stress cases. In the case with the mildest clamping ($\psi=0.46$), the model prediction is very close to the experimental data when the ceramic is far from reversal. However, the induced strain level close to reversal is quite far off. In this case, the prediction from the actuation strain assumption is much closer to the data. As the amount of clamping increases, the model prediction estimates the peak-to-peak strains better and better. One of the most important effects of clamping in the ceramics is that the inner edges of the butterfly loop straighten considerably as clamping increases. This effect is also well-modeled. The peak-to-peak value of the strain, as well as the shape of the butterfly loop as a whole, is much better approximated by the multiple-family model than by the actuation strain assumption.
Figure 4-14. Comparison of experimental strain and electrical displacement data from the sandwich structures with the predictions from the actuation strain assumption and from the multiple-family model. The points are the actual experimental data, dot-dash lines are from the actuation strain assumption, the solid lines are the model predictions based on the averaging method, and the dotted line are predictions based on the series expansion method.
Figure 4-15. Comparison of experimental strain and electrical displacement data from the sandwich structures with the predictions from the actuation strain assumption and from the multiple-family model. The points are the actual experimental data, dot-dash lines are from the actuation strain assumption, the solid lines are the model predictions based on the averaging method, and the dotted line are predictions based on the series expansion method.
d. Summary

These qualitative comparison of the model and data presented some very important knowledge about the model. While the material behavior close to polarization reversal is well-modeled in most of the cases, the lack of saturation mechanism is one of the major sources of discrepancy between the data and model prediction. However, such effect can be easily added to the model and does not pose a major problem. There are also some numerical problems associated with the simulations of the clamped cases. Other disagreements such as the amount of remanent polarization in clamped cases and dielectric permittivity will be further quantified in the following section. In general, the model provide a much better description of the material behavior under clamping at full reversal. The predictions of material behavior at intermediate field levels are not as satisfactory as in the high field cases.

4.3.2 Quantitative Comparisons

In order to clearly pinpoint the strength and weaknesses of the model, specific features of hysteresis and butterfly loops of the model predictions are compared to the experimental results. Many different choices of comparison are possible, and it is quite difficult for such study to be comprehensive due to the complexity of the material behavior. The following lists of comparisons are some of the more significant features that are potentially important to the actual application of the model. Since the calculation based on the series expansion method does not provide any meaningful results in cases with $\psi$ greater than 0.61, there are only three data points available in all the following comparisons.

a. Influence of Stress on Coercive Field

The coercive field is defined to be the field at which the electrical displacement vanishes when the ceramic is fully polarized. Thus, the value of the coercive field for different sandwich structures were obtained from the hysteresis loops with the maximum field at 944.9 V/mm. This is the highest applied field level and full polarization reversal is accomplished during every cycle of the applied field. The field at which the electrical displacement becomes zero was simply noted. Although there is a positive and a negative coercive field in each hysteresis loop, their magnitude should be equal since there is no inherent bias on the applied field. Thus, only the comparison of the positive coercive field is shown in Figure 4-16. It is interesting to note that the data show that while there is a slight increase in coercive field when the ceramic is clamped, the coercive field does not
vary significantly with the amount of clamping. This means that a clamped coercive field can be defined, which is slightly higher than the free coercive field. However, the model shows a different behavior. Although it is difficult to establish a trend for the series expansion method, the model using the averaging method clearly shows that the coercive field remain relatively unaffected by the presence of clamping on the ceramic. It is worth pointing out that the values of the model parameters that determine switching (means of energy barrier distributions) were chosen based on the coercive field of stress-free ceramic in §4.1.2. Thus, the good agreement on the data point \( \psi=0 \) is expected. In this case, although the disagreement is quite significant, the distinction between the clamped coercive field and the free coercive field is not very important. This is because when the applied field is so close to either one of the coercive fields, partial polarization reversal is bound to occur, as indicated in the sequence of simulation displayed in §4.3.1. Under these circumstances, quantitative predictions is extremely difficult and the such changes in the coercive becomes quite irrelevant. For applications such as poling, actual applied field is usually two to three times the coercive field, the significance of such distinction is further diminished.

Figure 4-16. Comparison of the coercive field vs relative stiffness obtained from experimental data and the multiple-family model.
b. Influence of Stress on Remanent Polarization

The remanent polarization is defined to be the amount of polarization remains in the ceramic after the applied field is removed. The exact amount of remanent polarization present in the ceramic depends on the history of the material states, which in turn depend on the input variables (applied field and stress). Comparison of remanent polarization is possible at any or at all the applied field levels used in the experiments. However, only comparison of remanent polarization in hysteresis loops undergoing full polarization reversal is meaningful. Since this represents the maximum attainable polarization in the ceramic, which signifies the maximum achievable alignment of the crystallites. The comparison is illustrated in Figure 4-17. There are some significant discrepancies throughout the whole range of $\psi$. The data show slight changes of remanent polarization as clamping increases, without any obvious trend. There is no satisfactory physical explanation for such behavior, except for variations of material properties and possible measurement errors introduced by the charge integrating circuit described in §2.2.2. However, the model shows altogether a different trend. As soon as clamping is applied, the remanent polarization decreased significantly. From a physical standpoint, since the clamping was applied in the transverse direction and the electrical displacement was measured in the longitudinal direction, clamping should not affect the remanent polarization at all. There is no adequate explanation for this model behavior either. One possible cause for this behavior is the method used to map the crystallite responses to the ceramic responses disregard the fact that the crystallites are bound by their neighbors. This will result in certain mismatch of boundary conditions on the crystallite surface, which may account for the extra charge. However, this is a pure speculation and should be examined more carefully to establish its validity.
c. Influence of Stress on Peak-to-Peak Strain

The comparison of the peak-to-peak strain produced at each field level provides a rough indication on the performance of the model in the larger scale. Figure 4-18 shows the comparison of the normalized peak-to-peak strain at two different field levels. The peak-to-peak strain from the data and the two methods were first normalized by the predicted levels from the actuation strain assumption. This will provide a clear picture to the merit of the different methods. When the maximum applied field was at 472.4 V/mm, full polarization reversal has not yet occurred. In the second case, when the maximum applied field was at 944.9 V/mm, the butterfly loop was already fully formed. As mentioned in the previous section, simulations of strain at high field and high clamping created some numerical problems, resulted in a very jagged responses with large spikes. Thus, error bars were placed in the last two data points in the high field case. The values of the peak-to-peak strain at those two points were calculated based on a least square fit of a fourth order polynomial of the strain signal ranging from the maximum field (the outer most tip of the
butterfly loop) up to the coercive field obtained from Figure 4-16 (the tail of the butterfly loop). The limits of the error bar were derived based on the actual strain signal from the simulations. From both plots of the normalized peak-to-peak strain, there is a common trend that the prediction by the actuation strain assumption is significantly higher than the measured values. This discrepancy between the data and the actuation strain assumption was discussed in Chapter 2. The predictions by the multiple-family model represent large improvements over the actuation strain assumption, but still higher than the measured values. Such disagreement in peak-to-peak strain is observed throughout the whole range of clamping. This is caused by the lack of saturation mechanism in the model. As it can be seen in the qualitative comparisons in the previous section, as the applied field increases towards the direction of the polarization, the actual field–strain relation curves away and produce less strain than the prediction of the linear model. However, the model does not demonstrate such effect and behave quite linearly when the applied field is in the direction of polarization. Thus, even though the model predicts the strain of the ceramic quite well when it is close to reversal, large discrepancies in the peak-to-peak strain are still present.
d. Influence of Stress on Dielectric Permittivity

One of the most significant features of the hysteresis loop is the slope of the loop near the remanent polarization. This slope represents the dielectric permittivity of the ceramic in its polarized state. The comparison of the dielectric permittivity derived from the hysteresis loops in the data and the model predictions are illustrated in Figure 4-19. Such measurement at two field levels are presented, at maximum field equals to 472.4 V/mm and 944.9 V/mm, respectively. As mentioned in the discussion of the peak-to-peak strain, full polarization reversal has not been achieved in the lower field level. Thus, the remanent
polarization was not present in the hysteresis loop. The dielectric permittivity was simply the slope of the hysteresis loop when the field vanishes. Since the clamping was not applied in the same direction as the electrical displacement was measured, the dielectric permittivity was not expected to change with clamping. Such expectation was reflected in the model behavior, with the predicted dielectric permittivity relatively unaffected by clamping. Experimental data show quite a different trend. The dielectric permittivity of the clamped ceramic tend to be lower than free ceramic. This seems to indicate that the direction of clamping is not very important. Since the small field clamped dielectric permittivity is usually much smaller than the free dielectric permittivity, it would seem that any application of clamping will change the dielectric permittivity. One possible physical explanation on the such a decrease is that the applied clamping decreases the mobility of ions in the lattice which are not completely perpendicular to the direction of the stresses.
e. Influence of Stress on Piezoelectric Strain Constant

The slope of the butterfly loop near zero field provides a measure of actuation capability available from the ceramic under different circumstances. When the ceramic is under stress-free conditions, this slope will be the piezoelectric strain constant $d_{31}$. However, when the ceramic is under clamping, the slope actually represents a weighted piezoelectric constant. This is because the stresses created by the clamping inhibits the free expansion of the ceramic, producing less strain. In the linear framework of the actuation strain assumption, the weighted piezoelectric constant can be derived from (2.15),
\[(d_{31})_{\text{weighted}} = \frac{d_{31}}{1 + \psi} \quad (4.12)\]

However, the ceramic behavior quickly becomes nonlinear at higher field, compound with the emergence of polarization reversal, such simple expression of the weighted piezoelectric constant can no longer be written. By direct measurement of the slope from the butterfly loops from the data, model prediction, and the actuation strain assumption, the comparison of the normalized weighted piezoelectric constant at two field levels are presented in Figure 4-20. As in the comparison of the peak-to-peak strain, the weighted piezoelectric constant from the data and model were first normalized by the predictions from the actuation strain assumption. The main distinction between the two field level is that while the full butterfly loop is already formed at the higher field level, the field–strain loop at the lower field level remains as a simple hysteresis loop. Thus, the weighted piezoelectric constant at that field level was simply a measure of the slope of the loop at zero field. The result is that there are only one set of curves for the low field level comparison. For the high field comparison, two sets of curves are presented because there is a slope associated with each of the direction of the polarization.

It can be easily seen that the prediction given by the multiple-family model is much closer to that given by the actuation strain assumption in all cases. The trend that the weighted piezoelectric constant decreases with increasing clamping is expected since higher clamping creates in higher opposing stress in the ceramic. The model behavior of the weighted piezoelectric constant is quite consistent with the behavior of the peak-to-peak strain. The model overpredicts both quantities, but still performs much better than the actuation strain assumption over the entire range of clamping.
Figure 4-20. Comparison of the normalized weighted piezoelectric constant at two field levels vs relative stiffness obtained from experimental data and the multiple-family model. All piezoelectric constant were normalized by the predictions from the actuation strain assumption.

**f. Stress–Strain Map at Constant Field Levels**

By utilizing all the full butterfly loops in different clamped cases from the data and the simulations, it possible to construct the stress–strain map containing a set of operating curves for the ceramic. This set of operating curves will provide valuable information on the high field behavior of PZT–5H under various stresses and fields. The set of curves were constructed as follows. First, the full butterfly loops (obtained at \( E_{\text{max}}=944.9 \text{ V/mm} \)) of all the clamped cases are shifted vertically on the strain axis so that the cross of the butterfly loop is centered at the origin, *i.e.*, when the applied field is zero, the strain is also
zero. This step is necessary because butterfly loops from different clamped cases have
different references of zero strain states in the experiment. To obtain a set of consistent
information of the material and model behavior, a common reference point must be set.
From these shifted butterfly loops, the strain at eight different field levels are recorded.
Since the butterfly loop is multiple-valued, the segment that was chosen to give the strains
is from the minimum field (lower left tip of the butterfly) to the positive coercive field
(upper right tip of the butterfly). This is illustrated in Figure 4-21. In this setting, positive
field is against the poling direction, whereas negative field is in the poling direction. For the
highly clamped cases where the simulations are quite noisy, a least square fit of a fourth
order polynomial to segment is used instead. This is the same procedure as the one used to
obtain the peak-to-peak strain in some cases. Finally, the stress at each field level and
clamping is obtained by using the perfect bonding assumption, i.e., the strain in the ceramic
is the same as the strain in the structure. Thus, the resultant stress in the ceramic is,

$$
T_p = \frac{-2c_s t_s}{t_p} S_p = \frac{-2c_s t_s}{t_p} S_p
$$

(4.13)

Then the stress–strain curves for a constant field is plotted for each of the field levels. Since
the clamping stress is always opposing the strain, the resultant curves will always lie on the
second and the fourth quadrant of the chart. The significance of each curve is similar to the
mechanical constitutive relation of the material at different field level. The slope of the
curve is then roughly the stiffness of the material at different stress and field levels.

![Figure 4-21. The points of measurements taken off the butterfly loops to construct the
operating curves. The crosses show the approximate locations of the data points taken off
the butterfly loop.](image)

The stress–strain maps constructed from the experimental data, the actuation strain
assumption, the multiple-family model based on the averaging method, and the series
expansion method are illustrated in Figure 4-22, Figure 4-23, Figure 4-24, and Figure 4-
25, respectively. Due to the limitations in the series expansion method, complete curves
that cover the whole range of clamping tested are not available. In the actuation strain assumption, since the linear assumptions that the stiffness of the material is constant and the material states are independent of stress, the operating curves in the stress–strain map in Figure 4-23 are entirely straight lines. This is of course not the true material behavior, which is illustrated in Figure 4-22. The most significant difference is that the operating curves are not straight lines. In addition, the stress level in all cases are significantly lower than that predicted by the actuation strain assumption, especially when the field is against the poling direction (positive field). Finally, there is a sudden drop in stress level in all the data points derived from the most clamped case ($\psi=12.16$). This is entirely unexpected and there is no satisfactory physical explanation to this unusual behavior. One possible cause is the shear experienced in the substrates and the bonding layer. However, one would expect such effect to surface quite gradually rather than in such abrupt manner.

The operating curves provided by the multiple-family model does not agree better with the data over the whole range of electric field (Figure 4-24). At the negative fields (in poling direction), the stress predicted is much higher than that of the data and the actuation strain assumption. The reason for this is again the lack of saturation mechanism in the model. This also results in the fact that the model actually behaves quite linearly in that field region, as the operating curves are quite close to be straight lines. Since the prediction of the actuation strain assumption is derived from the free strain data of the ceramic, certain amount of saturation effect at high field is already present. Thus, even the predicted stress is still higher than the stress from data, it is still closer than the model predictions.

However, at the positive fields (against poling direction), the model prediction is much closer than that of the actuation strain assumption. The predicted stress in that field region is actually lower than it is suppose to be. But the characteristic decrease of the slopes of the operating curves is captured in model. This again confirms the previous observation that the model captures the behavior of the ceramic very well when it is close to polarization reversal. Interestingly enough, the model also exhibits the same tendency of a sudden decrease in stress at the most clamped case, just like the actual data. It is not obvious in arriving at an explanation for such agreement between the data and the model. To determine whether this is a true material behavior, one will need additional data points with even higher clamping to expose the trend of the operating curves. However, simulation at such high degree of clamping will be particularly problematic.

Finally, the operating curves from the series expansion method displayed in Figure 4-25 do not provide sufficient data for an meaningful evaluation of the map. Nonetheless, it is still included for completeness.
Figure 4-22. The operating curves of PZT–5H constructed from experimental strain data.
Figure 4-23. The operating curves of PZT–5H constructed from predictions of the actuation strain assumption.
Stress-Strain Plots (Averaging Method)

Figure 4-24. The operating curves of PZT–5H constructed from predictions of the multiple-family model based on the averaging method.
Figure 4-25. The operating curves of PZT-5H constructed from predictions of the multiple-family model based on the series expansion method.

The following list summarizes the result of comparisons between the data and the model behavior.

- **Coercive Field**
  - Data: Increases slightly when clamped, remains quite constant $\psi$.
  - Model: Unaffected by clamping.

- **Remanent Polarization**
  - Data: Changes slightly with clamping without any obvious trend
  - Model: Decreases significantly when clamped, remains quite constant with $\psi$.  

150
• Peak-to-Peak Strain
  
  Data: Decrease faster than predicted by the actuation strain assumption with increasing $\psi$.
  
  Model: Slightly higher than data, but much closer to data than the actuation strain assumption for all cases.

• Dielectric Permittivity
  
  Data: Significant decrease when clamped, only slightly varied with $\psi$.
  
  Model: Relative unaffected by clamping.

• Weighted Piezoelectric Constant
  
  Data: Below the expectation of the actuation strain assumption.
  
  Model: Slightly higher than data, but much closer to data than the actuation strain assumption for all cases.

4.4 SUMMARY

In this chapter, the numerical values of all the model parameters were determined. There are primarily two types of model parameters. The first type is the parameters that are related to switching of polarization. Some of the switching parameters are determined by the material composition, while others are determined by trial and error. The second type of model parameters are the material constants of the crystallites, which describe the nominal behaviors of the crystallite, and the coefficients of the series expansion of the ceramic strain and electrical displacement. Most of the parameters were determined by using bisection method to fit the model responses to specific features of the hysteresis and butterfly loop of stress-free data. After a set of nominal values for the model parameters were obtained, an investigation to characterize the sensitivity of model behavior on some of the parameter variations was carried out.

The model with the set of nominal parameters was run to simulate the sandwich structures to obtain the electrical displacement and induced strain for comparison with the experimental results. However, additional modifications to the procedure of the simulation were needed in this case. Since the applied stress is proportional to the macroscopic strain and is not available explicitly as an input to the model simulation. Two methods were devised to estimate the induced stress in the ceramic. The first method is to use the strain level in the previous time step to calculate the stress level. This method was found to give diverging results when the relative stiffness, $\psi$, of the structure is greater than one. The second method is to directly impose equilibrium of a typical section as a constraint, and
then solve for the equilibrium stress through iteration. Since this method guarantees convergence, it was used in all subsequent simulations. In addition, an initialization procedure using an effective poling field was also developed to ensure that the model used in the simulations of the sandwich structures has the proper initial conditions.

Simulations were carried out for structures of six different values of $\psi$, and at six different field levels for each value of $\psi$. The results of the simulations were compared with the experimental data on both qualitative and quantitative basis. In the simulations of high clamping cases, some numerical problems were encountered that degrade the model prediction. In particular, the series expansion method was unable to operate at high clamping cases at all. In the comparisons, it was found that the model captures the material behavior particularly well near polarization reversal. On the other hand, the model did not capture the low field material behavior, as well as saturation effects at high field, when the applied field is in the direction of the polarization. The former is caused by the omission of domain wall movements in the modeling of crystallites, and the latter is due to the lack of a saturation mechanism due to the perfect piezoelectricity assumption in the crystallites. However, the saturation effect can be easily added into the model formulation and does not pose a serious problem. Other minor disagreements also appeared in the quantitative comparisons. However, the multiple-family model still provides much better predictions than the actuation strain assumption at higher $\psi$. On the other hand, the prediction of the dielectric response of the PZT is much closer to the experimental data. The shape and the details of the hysteresis loop were very well captured by the model prediction. The only exception is the amount of remanent polarization predicted for the clamped cases. However, the fact that the remanent polarization in all clamped cases remain quite uniform suggested that the fundamental behavior of the polarization is well-modeled, and most of the important effects related to polarization are captured.
Chapter 5: Conclusions and Recommendations

CONCLUSIONS

Due to the increasing demand for high authority actuators, commonly used ferroelectric actuators must operate at higher field and stress levels to accommodate the performance requirements. Under these circumstances, the nonlinear material behaviors of ferroelectrics, particularly polarization reversal, can no longer be ignored. Several nonlinear models that capture the various aspects of the nonlinear behavior of ferroelectric ceramics under high field and high stress were discussed. However, it was found that most of the currently available models are unsuitable for modeling actuators. The first reason is that most of these models were developed exclusively for crystals, and thus are not strictly applicable to bulk ceramics. A more important limitation of these models is that all of them were developed for stress-free conditions. There is no direct way to incorporate mechanical stress as an input to the system, in a way similar to electric field. Thus, the only way to use these models for stressed cases is by applying the actuation strain assumption to obtain the induced stress in the ferroelectric ceramic.

Two series of experiments were carried out to characterize the exact material behaviors in the operating regime of interest. The first series of tests was the low field characterization of the material. The experiments conducted were resonance tests outlined in the IRE Standards, to measure the material constants of the PZT-5H ceramic wafers used in all the experiments. The results from these tests were checked against the manufacturer's specifications to establish consistency in material quality and the reliability of the manufacturer's figures. In addition, the results from the resonant tests also provided some of the necessary data for the characterization of the model. The second series of experiments was the characterization of the high field behaviors of the material under various levels of stress. This was accomplished by examining the electromechanical responses of sandwich structures. The purpose of these experiments was to record the influences of the host structures having various extensional stiffnesses on the actuator performance. The test results were compared with the predictions made by the actuation strain assumption based on the stress-free behavior of the ceramic. It was conclusively shown that the actuation strain assumption overpredicted the induced strain level in all cases, even in the small field region. In the extreme case where the induced stress in the ceramic was the highest, the prediction from the actuation strain assumption was about twice the experimentally determined strain in the structure. A first order shear lag analysis
was also performed to determine the effect of bonding layers on the transmission of strain from the actuator to the structure. The results showed that the effect was negligible in all the sandwich structures used in the experiments.

Recognizing these limitations, a multiple-family model describing the nonlinear behaviors of polycrystalline ferroelectrics was developed. Since it is known that the primary cause behind all the important nonlinear behaviors is the occurrence of polarization reversal at high fields, the model is based on a description of the behavior of spontaneous polarization in the crystallites under the influences of simultaneously applied field and stress. Multiple families of internal variables are used to represent the random orientations of crystallites in the ceramic. A set of parameters that governs the switching behavior of the spontaneous polarization in the crystallite was assigned to each family. Upon determination of the state of polarization in the families for a given field and stress, this collection of material states can be used to calculate the ceramic responses. Two methods are derived for this purpose, the averaging method and the series expansion method. In the averaging method, a set of crystallite properties is assigned to each family to govern the nominal electromechanical behavior of the crystallite. The ceramic responses are then calculated by directly averaging all the properly rotated crystallite responses. In the series expansion method, instead of using the exact crystallite responses, the effective alignment of the crystallite about the polar axis is calculated. The ceramic responses are then represented by series expansions as functions of field, stress, and the effective alignment. Thus, the model is able to capture the polycrystalline nature of the material, as well as the stress dependence of the material states. Field and stress become the natural input into this model, with electrical displacement and strain as the output.

The multiple-family model was then implemented to simulate the behaviors of the sandwich structures in order to validate the performance of the model. The values for all the parameters appearing in the model were determined by matching the model outputs to the stress-free strain and electrical displacement of the PZT wafer. Based on this characterization of the model, an iterative method that directly enforces the equilibrium condition on the structure was used to determine the strain and electrical displacement histories for sandwiches with various relative stiffnesses. Although the strain predictions of the model were not as accurate as desired, most of the essential nonlinear behaviors were captured, especially when the system was close to full polarization reversal. In addition, the strain predictions of the multiple-family model were far superior to that of the actuation strain assumption model. The only exception is that the series expansion method was unable to produce reasonable results at high stress levels. Moreover, the predictions of the electrical displacement were better than the strain predictions. Almost all the nonlinear
behaviors were captured by the model, with the exception of the amount of remanent polarization in the stressed cases. Nonetheless, the behavioral trend of the electrical displacement for all the stressed cases remained consistent with physical observations. This indicates that the model of the quasi-static polarization behavior is substantially complete.

RECOMMENDATIONS

There are several aspects of this model that can be further improved. Currently, there are several problems encountered in this multiple-family model. The first is the need to assume unusually large material constants for the crystallites. The second is the large discrepancy in predicting the remanent polarization in the stressed cases. The third is insufficient accuracy and smoothness of strain predictions, especially in the high stress behavior of the model. All these problems are potentially related to the mapping between the microscopic and the macroscopic variables. At this point, all of the input and output variables are assumed to be equivalent in both the microscopic and macroscopic scale. This is in fact a very crude approximation. In real ceramics, the crystallites are tightly bound by neighboring crystallites. Under such conditions, both electric field and mechanical stress in the crystallite will have to satisfy certain boundary conditions on the surface of each crystallite. This basically becomes the problem of a piezoelectric body included in an effective anisotropic medium. For this problem, the interior loads on the crystallites can be calculated more accurately. Similarly, the presence of neighbors also prevents the crystallites from expanding freely. Such effects must be accounted for in order to accurately describe the responses of the macroscopic body.

The jaggedness of the strain response in the high stress situations is another manifestation of the inadequacy of the microscopic--macroscopic mapping. Under the current scheme, switching of one crystallite creates an extremely large strain. Thus, switching of a small number of crystallites in the model will represent a large macroscopic strain observed in the model. This effect is greatly magnified in the stressed cases due to the large induced stress in the structure. In actual crystallites, that kind of strain is never achieved due to the constraints imposed by the neighboring crystallites. Thus, a more reasonable method of imposing neighbor constraints and mapping microscopic strain to macroscopic strain is needed.

It is also important to add other time-dependent nonlinear effects neglected in the present development. Perhaps the most obvious omission is an aging mechanism. It is well-known that all ferroelectric material properties decay over time. Without this
mechanism, the model required the use of an effective poling field for initialization. While this is not a significant restriction on implementation, it is highly uncertain whether such an initial state obtained through this approach realistically represents the conditions in the ceramic. The inclusion of other nonlinear effects, such as saturation at high fields, will also improve the capabilities of the model.

Another area that can be improved is the modeling of the low field hysteresis that is caused mainly by domain wall movement. Crystallites in this multiple-family model are modeled as single-domain crystals. However, in material like PZT–5H, dopants are used to increase domain wall mobility. Thus, this effect is primary mechanism in creating hysteresis in the lower field region. Capturing such effects will drastically improve the model predictions in low field regions as well as in the transition region into full polarization reversal.

Besides fundamental features that can be added to the model, improvements are also needed in the implementation. First, a more sophisticated root searching algorithm is still needed to resolve closely spaced roots when enforcing the equilibrium condition of the structure during the simulation. Although uncertainty exists in choosing a proper metric to locate the “correct” root among all the possible equilibrium points, any minor improvement in this area will substantially improve the quality of strain predictions at high stress levels. Another obvious improvement can be made in the efficiency of the implementation. While the run time of the program that simulates the model still remains reasonable for high stress cases, when additional nested iterations are needed, it is virtually impossible to simultaneously implement multiple models in systems with multiple actuators.

In a larger scope, similar studies are desirable for other ferroelectric materials. Examination of materials such as hard PZT, which has a very different loss mechanism, can reveal the importance of various neglected nonlinear behaviors in relation to the polarization reversal-dependent hysteresis. These results may point to the direction in which additional modeling is needed to capture low field hysteresis.

Finally, with the capability of predicting the behavior of polarization in ferroelectric ceramics, it is possible to analyze systems beyond the simple configurations considered so far. With a properly implemented finite element version of this model, systems with spatially varying electric fields and polarization fields can be directly analyzed in detail for the first time. Another possibility is to directly exploit the large ferroelastic strain that is associated with 90° switching by accurately controlling the direction of polarization in the ceramic. Such large actuation strains will enable ferroelectrics to be used in applications never possible before.
Appendix A : Uncertainty Analysis

This appendix contains the complete uncertainty analysis of the resonance frequency test in determining the linear material properties of the PZT-5H wafers. The measurements made in the experiments were the thickness and the diameter of the disk, low frequency capacitance, the frequencies of maximum and minimum transmission and the minimum impedance of the ceramic. The sample of the test was comprised of five randomly chosen wafers. All the quantities were individually measured once, except for the capacitance, which were measured five times. Sources of uncertainties include least count errors of the instruments used, statistical fluctuations in multiple measurements and wafers, and uncertainties in the Poisson’s ratio. Complete uncertainty propagation was done for each individual wafer, and then the combine uncertainties of the sample was calculated. Since none of the sources of uncertainties were related, all the uncertainties were treated as independent in the subsequent calculations.

First, the uncertainty of the low frequency capacitance for each disk was calculated. Since the number of measurements taken for each disk is small, the Student’s t distribution was used to compute the confidence interval at 95% confidence level, as suggested in ANSI/ASME PTC 19.1-1985. The following equation was used to calculate the confidence interval.

\[ C_i = C_{\text{mean}}^i \pm t(0.95,5)S_c, \]  

(A1)

where \( C_i \) is the estimated capacitance of the \( i \)-th wafer, \( C_{\text{mean}}^i \) is the mean of the five measurements, \( S_c \) is the sample standard deviation and \( t(0.95,5) \) is the factor found in Table 10-5 of Reference 68. For confidence level of 95% and five measurements, \( t(0.95,5) = t_{1/2}(0.975, 4) = 2.78 \). A summary of the result is in the following table.

Table A-1. Summary of capacitance measurements and the associated uncertainties of the PZT disks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( C_{\text{mean}} ) (nF)</th>
<th>( \Delta C ) (nF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>47.68</td>
<td>0.1243</td>
</tr>
<tr>
<td>2</td>
<td>48.54</td>
<td>0.4652</td>
</tr>
<tr>
<td>3</td>
<td>48.62</td>
<td>0.5347</td>
</tr>
<tr>
<td>4</td>
<td>48.10</td>
<td>1.0945</td>
</tr>
<tr>
<td>5</td>
<td>48.00</td>
<td>1.2890</td>
</tr>
</tbody>
</table>

The capacitances of the unpoled disks were calculated in the same manner, and the result is summarized in the following table.
Table A-2. Summary of capacitance measurements and the associated uncertainties of the unpoled PZT disks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_{\text{mean}}$ (nF)</th>
<th>$\Delta C$ (nF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.88</td>
<td>0.3045</td>
</tr>
<tr>
<td>2</td>
<td>31.54</td>
<td>0.2487</td>
</tr>
</tbody>
</table>

The next step was to compute the uncertainties in the figure of merit $M$ given by (2.4). The the uncertainties calculated in Table A-1 was used as the uncertainties in capacitance. The least count of the multimeter was used as the uncertainties of $|Z_m|$. The uncertainties of the $f_m$ was ignored in all the calculations since the least count of the frequency counter is in orders of mHz, more than seven orders of magnitude smaller than the frequency measurements. The combined uncertainty of $M$ was propagated by the root sum square of the first order Taylor expansion of each variable.

$$
\Delta M = \left[ \left( \frac{\partial M}{\partial C} \Delta C \right)^2 + \left( \frac{\partial M}{\partial Z_m} \Delta Z_m \right)^2 \right]^{1/2},
$$

(A2)

$$
\Delta M = M \left[ \left( \frac{\Delta C}{C} \right)^2 + \left( \frac{\Delta Z_m}{Z_m} \right)^2 \right]^{1/2}.
$$

The uncertainty was then further propagated to the frequency difference $(f_p - f_s)$ by the same principle. The resulted equation for the uncertainty is then,

$$
\Delta (f_p - f_s) = \frac{4(f_p - f_s)}{M^3 + 4M}.
$$

(A3)

The numerical result of (A2) and (A3) are summarized in the following table.

Table A-3. Summary of the calculation results of the figure of merit $M$, the frequency difference $\Delta f$, and their uncertainties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M$</th>
<th>$\Delta M$</th>
<th>$\Delta f$ (kHz)</th>
<th>$\Delta(\Delta f)$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.4878</td>
<td>0.8053</td>
<td>16.3943</td>
<td>0.0103</td>
</tr>
<tr>
<td>2</td>
<td>16.3005</td>
<td>0.6705</td>
<td>13.9851</td>
<td>0.0127</td>
</tr>
<tr>
<td>3</td>
<td>18.0728</td>
<td>0.8105</td>
<td>16.2210</td>
<td>0.0109</td>
</tr>
<tr>
<td>4</td>
<td>17.6573</td>
<td>0.8383</td>
<td>16.5243</td>
<td>0.0119</td>
</tr>
<tr>
<td>5</td>
<td>15.6240</td>
<td>0.7148</td>
<td>15.9201</td>
<td>0.0164</td>
</tr>
</tbody>
</table>

Since $k_p$ given by (2.6) is a complicated function of two Bessel functions in addition to the uncertainty in $v^6$, the uncertainties was calculated in several steps. First define,
\[ x(\Delta f) = \eta_l(1 + \Delta f / f_m), \]
\[ \alpha(x) = \frac{J_1(x)}{xJ_0(x)}, \]

then (2.6) can be written as,
\[ k_p^2 = \frac{(1 - v^E)\alpha(x) - 1}{2\alpha(x) - 1}. \] (A4)

By using the fact that,
\[ \frac{dJ_0(x)}{dx} = -J_1(x) \; ; \; \frac{dJ_1(x)}{dx} = J_0(x) - \frac{1}{x} J_1(x), \]
the final uncertainty, including that of the frequency difference and the Poisson’s ratio is given by (A5). The range of Poisson’s ratio was taken to be \( v^E = 0.31 \pm 0.02. \)
\[ \Delta k_p = \sqrt{(\Delta k_p|_{\Delta f})^2 + (\Delta k_p|_{v^E})^2}, \] (A5)
where,
\[ \Delta k_p|_{\Delta f} = \frac{(1 + v^E)[(1 - \alpha/x) + \alpha]}{2k_p(2\alpha - 1)^2 x} \Delta(f_p - f_s), \]
\[ \Delta k_p|_{v^E} = \frac{1}{2k_p} \left( \frac{\alpha}{2\alpha - 1} \right) \Delta v^E. \]

Similarly, the uncertainty in \( k_{31} \) is given by the (A6) and the numerical results are summarized in Table A-3.
\[ \Delta k_{31} = \left[ \frac{(k_p\Delta v^E)^2}{2(1 - v^E)} + \frac{(1 - v^E)}{2} \left( \Delta k_p \right)^2 \right]. \] (A6)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( k_p )</th>
<th>( \Delta k_p )</th>
<th>( k_{31} )</th>
<th>( \Delta k_{31} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6362</td>
<td>0.007</td>
<td>0.3737</td>
<td>0.012</td>
</tr>
<tr>
<td>2</td>
<td>0.5923</td>
<td>0.008</td>
<td>0.3479</td>
<td>0.011</td>
</tr>
<tr>
<td>3</td>
<td>0.6329</td>
<td>0.007</td>
<td>0.3717</td>
<td>0.012</td>
</tr>
<tr>
<td>4</td>
<td>0.6394</td>
<td>0.007</td>
<td>0.3756</td>
<td>0.012</td>
</tr>
<tr>
<td>5</td>
<td>0.6288</td>
<td>0.007</td>
<td>0.3694</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table A-4. Summary of calculation results of the coupling factors and their uncertainties.

Finally, all the equations for propagation of uncertainties into the three material constants can be derived from (2.7), and they are as follows. Summary of numerical results are shown in Table A-5.
\[ \Delta e_{33}^T = e_{33}^T \left[ \left( \frac{\Delta C}{C} \right)^2 + \left( \frac{\Delta d}{d} \right)^2 + \left( \frac{\Delta t}{t} \right)^2 \right]^{1/2}, \]

\[ \Delta s_{11}^E = s_{11}^E \left[ \left( \frac{\Delta V^E}{V^E} \right)^2 + \left( 2 \frac{\Delta d}{d} \right)^2 \right]^{1/2}, \]

\[ \Delta d_{31} = d_{31} \left[ \left( \frac{\Delta k_p}{k_p} \right)^2 + \left( \frac{\Delta e_{33}^T}{2 e_{33}^T} \right)^2 + \left( \frac{\Delta s_{11}^E}{2 s_{11}^E} \right)^2 \right]^{1/2}. \]  

(A7)

Table A-5. Summary of calculation results of the material constants of the PZT disks and their uncertainties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( s_{11} ) (m²/N)</th>
<th>( \Delta s_{11} ) (m²/N)</th>
<th>( d_{31} ) (m/V)</th>
<th>( \Delta d_{31} ) (m/V)</th>
<th>( e_{33} ) (F/m²)</th>
<th>( \Delta e_{33} ) (F/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.575×10⁻¹¹</td>
<td>1.016×10⁻¹²</td>
<td>2.553×10⁻¹⁰</td>
<td>1.25×10⁻¹¹</td>
<td>2.964×10⁻⁸</td>
<td>1.187×10⁻⁹</td>
</tr>
<tr>
<td>2</td>
<td>1.520×10⁻¹¹</td>
<td>0.981×10⁻¹²</td>
<td>2.325×10⁻¹⁰</td>
<td>1.17×10⁻¹¹</td>
<td>2.937×10⁻⁸</td>
<td>1.224×10⁻⁹</td>
</tr>
<tr>
<td>3</td>
<td>1.559×10⁻¹¹</td>
<td>1.006×10⁻¹²</td>
<td>2.495×10⁻¹⁰</td>
<td>1.23×10⁻¹¹</td>
<td>2.890×10⁻⁸</td>
<td>1.204×10⁻⁹</td>
</tr>
<tr>
<td>4</td>
<td>1.583×10⁻¹¹</td>
<td>1.021×10⁻¹²</td>
<td>2.576×10⁻¹⁰</td>
<td>1.26×10⁻¹¹</td>
<td>2.972×10⁻⁸</td>
<td>1.189×10⁻⁹</td>
</tr>
<tr>
<td>5</td>
<td>1.559×10⁻¹¹</td>
<td>1.006×10⁻¹²</td>
<td>2.509×10⁻¹⁰</td>
<td>1.23×10⁻¹¹</td>
<td>2.960×10⁻⁸</td>
<td>1.184×10⁻⁹</td>
</tr>
</tbody>
</table>

The analysis for the compliance and the dielectric permittivity follows a similar procedure. While the computation for the uncertainties for \( e \) is the same as that for \( e_{33} \), computation for \( s \) and \( \Delta s \) requires an extra step. Since the actual compliance measurements carried out with the unpoled samples are the composite disks, the above measurements on the active disks must be used to calculate the compliance of the unpoled disks by using (2.8). However, when (2.8) is used to derive the equation for the uncertainty of \( s \), the uncertainties from the two compliance terms must be added directly instead of using the root sum square method. This is because the source for both compliance measurements are not independent of each other; they are actually the same. Thus, the uncertainty for the compliance of the unpoled disks is

\[ \Delta s_{11}^{unpoled} = 2 \Delta s_{11}^{comp} - \Delta s_{11}^E. \]  

(A8)

The results of the analysis on the unpoled disks are summarized in the following table.
Table A-6. Summary of calculation results of the material constants of the unpoled PZT disks and their uncertainties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( s \ (m^2/N) )</th>
<th>( \Delta s \ (m^2/N) )</th>
<th>( \varepsilon \ (F/m^2) )</th>
<th>( \Delta \varepsilon \ (F/m^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.381\times10^{-11}</td>
<td>8.910\times10^{-13}</td>
<td>1.920\times10^{-8}</td>
<td>7.679\times10^{-10}</td>
</tr>
<tr>
<td>2</td>
<td>1.405\times10^{-11}</td>
<td>9.067\times10^{-13}</td>
<td>1.909\times10^{-8}</td>
<td>7.953\times10^{-10}</td>
</tr>
</tbody>
</table>

The final uncertainty of each quantity is the combined uncertainties from the propagated experiment uncertainties, \( b_x \), and the contribution from statistical fluctuation, \( p_x \). The former is approximated by the average of the uncertainties over five wafers and the latter was estimated by the standard deviation of the mean. Then they are combined, again using root sum square of the two uncertainties. Thus, the total uncertainty is given by,

\[
\Delta x = \sqrt{b_x^2 + p_x^2},
\]

and \( p_x = \frac{t(0.95,5)S_x}{\sqrt{N}} \). The final results are summarized in Table A-7.

Table A-7. Summary of the results of the uncertainty analysis of the resonance tests.

<table>
<thead>
<tr>
<th>( \varepsilon_{33} \ (F/m^2) )</th>
<th>Mean</th>
<th>Total uncertainty</th>
<th>Percentage Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.945\times10^{-8}</td>
<td>1.267\times10^{-9}</td>
<td>4.302</td>
<td></td>
</tr>
<tr>
<td>( \varepsilon \ (F/m^2) )</td>
<td>1.914\times10^{-8}</td>
<td>8.275\times10^{-10}</td>
<td>4.323</td>
</tr>
<tr>
<td>( k_p )</td>
<td>0.6259</td>
<td>0.0250</td>
<td>3.997</td>
</tr>
<tr>
<td>( k_{31} )</td>
<td>0.3677</td>
<td>0.0182</td>
<td>4.938</td>
</tr>
<tr>
<td>( s_{11} \ (m^2/N) )</td>
<td>1.559\times10^{-11}</td>
<td>1.049\times10^{-12}</td>
<td>6.730</td>
</tr>
<tr>
<td>( s \ (m^2/N) )</td>
<td>1.393\times10^{-11}</td>
<td>8.989\times10^{-13}</td>
<td>6.452</td>
</tr>
<tr>
<td>( d_{31} \ (m/V) )</td>
<td>2.492\times10^{-10}</td>
<td>1.738\times10^{-11}</td>
<td>6.974</td>
</tr>
<tr>
<td>( M )</td>
<td>17.2285</td>
<td>1.6960</td>
<td>9.844</td>
</tr>
</tbody>
</table>
Appendix B: Source Code for Model Simulation

The following is the source code for the program written for the simulation of the model. It was written in C and compiled on an IBM POWERStation 320 running RS/IX 7.6H. The following text that is in this include <stdlib.h> type of typeface are part of the original source code, while the regular typeface are comments added in this section to explain the code.

```c
#include <stdlib.h>
#include <stdio.h>
#include <math.h>

#define MAXT 1000
#define MAXPHI 40
#define MAXPSI 40
#define MAXN 1600
#define PI 3.141592654

#define SIGN(a,b) ((b) >= 0.0 ? fabs(a) : -fabs(a))
#define MIN(a,b) (((a) > (b) ? (b) : (a))
#define sig(a) ((a) >= 0 ? (1) : -(1))

void stordoub(double *arr, FILE *fp, char *pname);

/**** Declaration of data type ****/
typedef double rmat[MAXPHI][MAXPSI][3][3];
typedef double umat[MAXPHI][MAXPSI][6][6];
typedef double mat[MAXPHI][MAXPSI];
typedef double stress[MAXPHI][MAXPSI][6];
typedef double field[MAXPHI][MAXPSI][3];
typedef double compl[6][6][6];
typedef double piezo[6][6][3];
typedef double diele[6][3][3];
typedef struct {
    long type;
    long mrows;
    long mcols;
    long imagf;
    long namlen;
} Fmatrix;

/**** Declare function pointer ****/
static void (*Strain)();

/**** Declaration of global variables ****/
int nPHI,nPSI,Step,flagT;
double Up,Ud,Us,Ps,Sc,tp,tol,ptol,micro[13],macro[6];
double rUp,rUd,rUs,gam,Ntm[MAXT],Ndm[MAXT];
```
The following routine setup() is used to generate the required time and sinusoidal electric field vector. The two Euler angles for all the families and their associated rotation matrices are also generate.

```c
void setup(double *E, double tf, double Ae, double w,
  double *phi, double *psi)
{
  register int i,j;
  double  cosphi[MAXPHI], sinphi[MAXPHI],
         cospsi[MAXPSI], sinpsi[MAXPSI];
  double  t[MAXT];

  /*** Generate time and electric field vectors ***/
  for (i=0 ; i<Step ; i++)
  {
    t[i]=i*tf/Step;
    E[i]=Ae*sin(2*PI*w*t[i]);
  }

  /*** Generate Euler angle vectors ***/
  for (i=0; i<nPHI ; i++)
  {
    phi[i]=(2*i+1)*PI/(2*nPHI);
    cosphi[i]=cos(phi[i]);   sinphi[i]=sin(phi[i]);
  }
  for (i=0; i<nPSI; i++)
  {
    psi[i]=(2*i+1)*PI/(4*nPSI);
    cospsi[i]=cos(psi[i]);   sinpsi[i]=sin(psi[i]);
  }

  /*** Generate weighting function ***/
  for (i=0 ; i<nPHI ; i++)
    for (j=0 ; j<nPSI ; j++)
      mu[i][j]=0.5*sinphi[i]*PI/nPHI/nPSI;

  /*** Generate rotation matrices ***/
  for (i=0 ; i<nPHI ; i++)
```
for (j=0 ; j<nPSI ; j++)
{
    Rot[i][j][0][0]=cosphi[i]*cospsi[j];
    Rot[i][j][0][1]= -cosphi[i]*sinpsi[j];
    Rot[i][j][0][2]=sinphi[i];
    Rot[i][j][1][0]=sinpsi[j];
    Rot[i][j][1][1]=cospsi[j];
    Rot[i][j][1][2]=0;
    Rot[i][j][2][0]= -sinphi[i]*cospsi[j];
    Rot[i][j][2][1]=sinphi[i]*sinpsi[j];
    Rot[i][j][2][2]=cosphi[i];
}

The material constants for the crystallites in all six different polarization configuartions are
generated in the following routine pack().

void pack()
{
    register int  i;
    double *sptr,*dptr,*eptr;
    double s11,s12,s13,s33,s44,s66,d31,d32,d15,e1,e3;

    sptr=&(slocal[0][0][0]);
    for (i=0 ; i<216 ; i++)
        *(sptr+i)=0.0;
    s11=micr0[0]; s12=micr0[1]; s13=micr0[2]; s33=micr0[3];
    s44=micr0[4]; s66=micr0[12]; d31=micr0[7]; d32=micr0[8];
    d15=micr0[9]; e1=micr0[5]; e3=micr0[6];

    //*** compliance with polar axis in 1 ***/
    slocal[0][0][0]=s33; slocal[0][0][1]=s13;
    slocal[0][0][2]=s13; slocal[0][1][0]=s13;
    slocal[0][1][1]=s11; slocal[0][1][2]=s12;
    slocal[0][2][0]=s13; slocal[0][2][1]=s12; slocal[0][2][2]=s11;
    slocal[0][3][3]=s66;
    slocal[0][4][4]=s44; slocal[0][5][5]=s44;

    //*** compliance with polar axis in 2 ***/
    slocal[1][0][0]=s11; slocal[1][0][1]=s13;
    slocal[1][0][2]=s12; slocal[1][1][0]=s13;
    slocal[1][1][1]=s33; slocal[1][1][2]=s13;
    slocal[1][2][0]=s12; slocal[1][2][1]=s13; slocal[1][2][2]=s11;
    slocal[1][3][3]=s44;
    slocal[1][4][4]=s66; slocal[1][5][5]=s44;

    //*** compliance with polar axis in 3 ***/
    slocal[2][0][0]=s11; slocal[2][0][1]=s12;
    slocal[2][0][2]=s13; slocal[2][1][0]=s12;
    slocal[2][1][1]=s11; slocal[2][1][2]=s13;
    slocal[2][2][0]=s13; slocal[2][2][1]=s13;
    slocal[2][2][2]=s33; slocal[2][3][3]=s44;
    slocal[2][4][4]=s44; slocal[2][5][5]=s66;

    for (i=0 ; i<108 ; i++)
        *(sptr+108+i)=*(sptr+i);
```c

dptr=&(dlocal[0][0][0]);
for (i=0 ; i<54 ; i++)
  *(dptr+i)=0.0;

/*** Piezo constant with polar axis in 1 ***/
dlocal[0][0][2]=d33; dlocal[0][1][2]=d31;
dlocal[0][2][2]=d31; dlocal[0][4][0]=d15;
dlocal[0][5][1]=d15;

/*** Piezo constant with polar axis in 2 ***/
dlocal[1][0][2]=d31; dlocal[1][1][2]=d33;
dlocal[1][2][2]=d31; dlocal[1][3][1]=d15;
dlocal[1][5][0]=d15;

/*** Piezo constant with polar axis in 3 ***/
dlocal[2][0][2]=d31; dlocal[2][1][2]=d31;
dlocal[2][2][2]=d33; dlocal[2][3][1]=d15;
dlocal[2][4][0]=d15;

for (i=0 ; i<54 ; i++)
  *(dptr+54+i)=-(*(dptr+i));

eptr= &((e0[0][0][0];
for (i=0 ; i<54 ; i++)
  *(eptr+i)=0.0;

/*** Dielectric constant with polar axis in 1 ***/
e0[0][0][0]=e3; e0[0][1][1]=e1;
e0[0][2][2]=e1;

/*** Dielectric constant with polar axis in 2 ***/
e0[1][0][0]=e1; e0[1][1][1]=e3;
e0[1][2][2]=e1;

/*** Dielectric constant with polar axis in 3 ***/
e0[2][0][0]=e1; e0[2][1][1]=e1;
e0[2][2][2]=e3;

for (i=0 ; i<27 ; i++)
  *(eptr+27+i)= *(eptr+i);
}

#define IA 16807
#define IM 2147483647
#define AM (1.0/IM)
#define IQ 127773
#define IR 2836
#define NTAB 32
#define NTV (1+(IM-1)/NTAB)
#define EPS 1.2e-7
#define RNMX (1.0-EPS)
```

The following two routine ran1() and gdev() are directly from Reference 67. ran1() is used to generate a random number sequence with uniform distribution between 0 and 1.
gdev() then uses the output of ran1() to generate a normally distributed random number sequence with zero mean and unit variance.

float ran1(long *idum)
{
    register int j;
    long k;
    static long iy=0;
    static long iv[NTAB];
    float temp;

    if (*idum <= 0 || !iy) {
        if (1>(*idum) < 1) *idum=1;
        else *idum = -(idum);
        for (j=NTAB+7; j>=0; j--) {
            k=(*idum)/IQ;
            *idum=IA*(idum-k*IQ)-IR*k;
            if (*idum < 0) *idum += IM;
            if (j < NTAB) iv[j] = *idum;
        }
        iy=iv[0];
    }
    k=(*idum)/IQ;
    *idum=IA*(idum-k*IQ)-IR*k;
    if (*idum < 0) *idum += IM;
    j=i/y/NDIV;
    iy=iv[j];
    iv[j] = *idum;
    if ((temp=AM*i/y) > RNMX) return RNMX;
    else return temp;
}

float gdev(long *idum)
{
    float ran1(long *idum);
    static int iset=0;
    static float gset;
    float fac,rsq,v1,v2;

    if (iset == 0) {
        do {
            v1=2.0*ran1(idum)-1.0;
            v2=2.0*ran1(idum)-1.0;
            rsq=v1*v1+v2*v2;
        } while (rsq >= 1.0 || rsq == 0.0);
        fac=sqrt(-2.0*log(rsq)/rsq);
        gset=v1*fac;
        iset=1;
return v2*fac;
} else {
    iset=0;
    return gset;
}

The following routine energy() generate the set of normally distributed energy barriers for each of the family

void energy()
{
    register int i,j;
    static int Ind[36]={0,1,4,2,1,4,
        1,0,4,1,2,4,
        3,3,0,3,3,2,
        2,1,4,0,1,4,
        1,2,4,1,0,4,
        3,3,2,3,3,0};
    long seed=234567374;
    double U[MAXN][5];
    double U180,U90,Ur;
    double *Utotptr,*Uptr;

    Utotptr= &((tot[0][0][0][0]);
    Uptr= &((U[0][0]);

    /*** Generate switching energy barriers ***/
    Ud=Up-Us;
    for (i=0 ; i<(nPHI*nPSI) ; i++)
    {
        U90=(Ud+Ud*gdev(&seed))*1000;
        U180=(Up+Up*gdev(&seed))*1000;
        Ur=(Us+Us*gdev(&seed))*1000;
        U[i][0]=0; U[i][1]=U90; U[i][2]=U180;
        U[i][3]=U90+Ur; U[i][4]=U90-gam*Ur;
    }

    for (i=0 ; i<(nPHI*nPSI) ; i++)
    for (j=0 ; j<36 ; j++)
        *(Utotptr+(i*36)+j)= *(Uptr+i*5+Ind[j]);
}

void work()
{

    /*** This routine assumes the electrical loading to be ***/
    /*** aligned only in 3-axis and the mechanical loading ***/
    /*** to be planar in 1-2 plane with Tr=const. All the ***/
    /*** possible work done for each family is calculated ***/
    /*** and put in form of 6x6 matrices. ***/

    register int i,j,k,l;
    double P2[MAXPHI][MAXPSI][6],P3[6][6];
    double S2[MAXPHI][MAXPSI][6],S3[6][6];

    for (i=0 ; i<nPHI ; i++)
for (j=0 ; j<nPSI ; j++)
{
    for (k=0 ; k<3 ; k++)
    {
        P2[i][j][k]=Rot[i][j][2][k];
        P2[i][j][k+3]=-P2[i][j][k];
        S2[i][j][k]=1-pow(Rot[i][j][2][k],2.0);
        S2[i][j][k+3]=S2[i][j][k];
    }

    for (k=0 ; k<6 ; k++)
        for (l=0 ; l<6 ; l++)
        {
            P3[k][l]=P2[i][j][l];
            S3[k][l]=S2[i][j][l];
        }

    for (k=0 ; k<5 ; k++)
        for (l=0 ; l<6 ; l++)
        {
            We[i][j][k][l]=Ps*(P3[k][l]-P3[l][k]);
            Wm[i][j][k][l]=Sc*(S3[k][l]-S3[l][k]);
        }
}

void calload()
{
    register int i,j;

    /*** Calculate unit load of stress, field in local frames ***/
    for (i=0 ; i<PHI ; i++)
        for (j=0 ; j<nPSI ; j++)
        {
            /*** Component by component tensor transform of ***/
            /*** field from global to local coordinates ***/
            uTl[i][j][0]=(1-pow(Rot[i][j][2][0],2.0));
            uTl[i][j][1]=(1-pow(Rot[i][j][2][1],2.0));
            uTl[i][j][2]=(1-pow(Rot[i][j][2][2],2.0));
            uTl[i][j][3]=-Rot[i][j][2][1]*Rot[i][j][2][2];
            uTl[i][j][4]=-Rot[i][j][2][0]*Rot[i][j][2][2];
            uTl[i][j][5]=-Rot[i][j][2][0]*Rot[i][j][2][1];

            /*** Component by component vector transform of ***/
            /*** field from global to local coordinates ***/
            uEl[i][j][0]=Rot[i][j][2][0];
            uEl[i][j][1]=Rot[i][j][2][1];
            uEl[i][j][2]=Rot[i][j][2][2];

            /*** Component by component tensor transform of strain ***/
            /*** sl1 from local to global coordinates ***/
            uS1g1[i][j][0]=pow(Rot[i][j][0][0],2.0)*
                           pow(Rot[i][j][1][0],2.0);
            uS1g1[i][j][1]=pow(Rot[i][j][0][1],2.0)*
                           pow(Rot[i][j][1][1],2.0);
            uS1g1[i][j][2]=pow(Rot[i][j][0][2],2.0)*
                           pow(Rot[i][j][1][2],2.0);
            uS1g1[i][j][3]=Rot[i][j][0][1]*Rot[i][j][0][2]+
This routine uses the current electric field, stress and crystallite states and calculate the next crystallite states and the resultant macroscopic strain based on the rule derived from the principle of minimum potential energy. In the cases where the initial is provided as an input, it will be subtracted out. The resultant strain is then calculated based on the series expansion method.

void sswitchcm(double E, double T, int *Ni, int *Nf, double *Scm, double Scm0, double *Nt, double *Nd)
{
    register int i,j;
    int row,nextP;
    double Nglobal,Np;
    double minPot,Pot[6],*Uotptr,*Weptr,*Wmptr,
        *muptr,*Rotptr;

    Uotptr= &(Uot[0][0][0][0]); Weptr= &(We[0][0][0][0]);
    Wmptr= &(Wm[0][0][0][0]); muptr= &(mu[0][0]);
    Rotptr= &(Rot[0][0][0][0]);

    /*** Initialize variables ***/
    *Scm=0.0; Np=0.0; *Nt=0.0; *Nd=0.0;
    for (i=0 ; i<(nPHI*nPSI) ; i++)
    {
        Nf[i]=Ni[i];

        /*** Form total PE based on previous state ***/
        row=i*36+Nf[i]*6;
        for (j=0 ; j<6 ; j++)
            Pot[j]=(*Uotptr+row+j)-(*Weptr+row+j))*E
                -(*Wmptr+row+j))*T;

        /*** Search for next position ***/
        nextP=0; minPot=Pot[0];
        for (j=1 ; j<6 ; j++)
            if (Pot[j]<minPot) { nextP=j; minPot=Pot[j];}
        if (minPot<0.0) Nf[i]=nextP;

        /*** Calculate polarization in global coordinates ***/
Nglobal=0.0;
for (j=0 ; j<3 ; j++)
    Nglobal= *(Rotptr+i*9+6+j)*basis[j][Nf[i]]+Nglobal;

///** Calculate effective N ***/    
if ((Nf[i]==2)||(Nf[i]==5))
    Np=Np+Nglobal*(*(muptr+i));
else
    *Nd=*Nd+Nglobal*(*(muptr+i));
    *Nt=Np+ *Nd;
}
*Scm=(macro[0]+macro[1]*fabs(*Nt))*T+macro[2]*(*Nt)*E
    -macro[3]*fabs(*Nd)-Scm0;

This routine uses the current electric field, stress and crystallite states and calculate the next crystallite states and the resultant macroscopic strain based on the rule derived from the principle of minimum potential energy. In the cases where the initial is provided as an input, it will be subtracted out. The resultant strain is then calculated based on the averaging method.

void sswitch(double E, double T, int *Ni, int *Nf, double *S1,
    double S10, double *Nt, double *Nd)

    /*** Variables Nt, Nd are not used in this function ***/     
    /*** They are passed to conform to the function           
    /*** pointer format for the two strain routines          
    
{
    register int i,j,k;
    int row,nextP;
    double minPot,Sv[6],Pot[6],Sgl1;
    double *Utotptr,*Weptr,*Wmptr,*muptr,*uTlptr,
    *uElptr,*uSlglptr;

    Utotptr= &(Utot[0][0][0][0][0][0]); Weptr= &(We[0][0][0][0][0][0]);
    Wmptr= &(Wm[0][0][0][0][0][0]); uSlglptr= &(uSlgl[0][0][0][0][0][0]);
    uTlptr= &(uTl[0][0][0][0][0][0]); uElptr= &(uEl[0][0][0][0][0][0]);
    muptr= &(mu[0][0][0][0][0][0]);

    /*** Initialize variables ***/    
    *S1=0.0;
    for (i=0 ; i<(nPHI*nPSI) ; i++)
    {
    Nf[i]=Ni[i];

    /*** Form total PE based on previous state ***/     
    row=i*36+Nf[i]*6;
    for (j=0 ; j<6 ; j++)
        Pot[j]=(*(Utotptr+row+j))-(*(Weptr+row+j))*E-
            (*(Wmptr+row+j))*T;

    /*** Search for next position ***/      
    nextP=0; minPot=Pot[0];
    for (j=1 ; j<6 ; j++)
    
171
if (Pot[j]<minPot) {nextP=j; minPot=Pot[j];}
if (minPot<=0) Nf[i]=nextP;

/*** Calculate Strain tensor in local coordinates ***/
for (j=0 ; j<6 ; j++) Sv[j]=0.0;
for (j=0 ; j<6 ; j++)
    for (k=0 ; k<6 ; k++)
        Sv[j]=slocal[Nf[i]][j][k]*(*(uTlptr+i*6+k))*T
        +Sv[j];
/*** (*uTlptr+i*6+k)*T is the local stress ***/

for (j=0 ; j<6 ; j++)
    Sv[j]=Sv[j]+*(uElptr+i*3)*E*dlocal[Nf[i]][j][0]
    +(uElptr+i*3+1)*E*dlocal[Nf[i]][j][1]+
    *(uElptr+i*3+2)*E*dlocal[Nf[i]][j][2]+
    Sv[j]+Sc*sd[j][Nf[i]];
/*** *(uElptr+i*3+k)*E is the local field ***/

/*** Calculate average Strain in global coordinates ***/
Sgll=0.0;
for (j=0 ; j<6 ; j++)
    Sgll=Sgll+ *(uSglptr+i*6+j)*Sv[j];
*S1= *S1+Sgll*(*(mu.ptr+i))/2;
}
*S1= *S1-S10;
}

This routine uses the current electric field, stress and crystallite states and calculate the resultant macroscopic electrical displacement by averaging all the crystallite electrical displacements.

double electdisp(double E, double T, int *N)
{
    register int i,j,k;
    double D,Dlocal[3],Dgl,*muptr,*uElptr,
    *uTlptr,*Rotptr;

    muptr= &(mu[0][0][0]); uElptr= &(uEl[0][0][0][0]);
    uTlptr= &(uTl[0][0][0][0]); Rotptr=&(Rot[0][0][0][0][0]); D=0.0;

    /*** Calculate D3 for ceramic for given loads and states ***/
    for (i=0 ; i<nPHI*nPSI ; i++)
    {
        Dlocal[0]=0.0; Dlocal[1]=0.0; Dlocal[2]=0.0;
        for (j=0 ; j<3 ; j++)
            for (k=0 ; k<6 ; k++)
                Dlocal[j]=dlocal[N[i]][j][k]*
                (*uTlptr+i*6+k)*T+Dlocal[j];
        for (j=0 ; j<3 ; j++)
            Dlocal[j]=Dlocal[j]+Ps*basis[j][N[i]]+
            *(uElptr+i*3+j)*E*elocal[N[i]][j][j];
        Dgl=*(Rotptr+i*9+6)*Dlocal[0]+
        *(Rotptr+i*9+7)*Dlocal[1]+
        *(Rotptr+i*9+8)*Dlocal[2];
        D=D+Dgl*(*(muptr+i));
    }
}
return D;
}

The following routine is a modification of the routine of the Ridder’s method provided in Reference 67. This is routine is called from the time loop instead of sswitch() if the structural thickness is nonzero. This routine will call sswitch() during each iteration until an equilibrium is reached.

#define NRANSI
#define MAXIT 20
#define UNUSED (-1.11e30)

double zriddr(double E, int *Ni, int *Nf, double Ti,
   double *S1, double S10, double Sprev,
   double *Nt, double *Nd)
{
   int j;
   double ans,gh,gl,gm,gnew,s,xh,xl,xm,xnew;
   double T1,T2,bs11,bs12,Cs,ts,Nt,Nd;

   Cs=micro[10]; ts=micro[11];
   /*** First, bracket the root by T1, T2 ***/
   bs11=0.0; T1=Ti;
   (*Strain)(E,T1,Ni,Nf,&bs11,S10,&Nt,&Nd);
   /*** First function evaluation at bracket 1 ***/
   gl=bs11-Sprev;
   T2=Ti-Cs*te*gl/tp; bs12=0.0;
   (*Strain)(E,T2,Ni,Nf,&bs12,S10,&Nt,&Nd);
   /*** Second function evaluation at bracket 2 ***/
   gh=bs12+T2*tp/Cs/ts;

   if (gl==0.0) return T1;
   if (gh==0.0) return T2;

   while (sig(gl) == sig(gh))
   {
      if (fabs(gh) > fabs(gl))
         /*** T1 is always > T2 ***/
         {
            T1=T1+fabs(Cs*ts*gl/tp);
            (*Strain)(E,T1,Ni,Nf,&bs11,S10,&Nt,&Nd);
            gl=bs11+T1*tp/Cs/ts;
         }
      else
         {
            T2=T2-fabs(Cs*ts*gl/tp);
            (*Strain)(E,T2,Ni,Nf,&bs12,S10,&Nt,&Nd);
            gh=bs12+T2*tp/Cs/ts;
         }
   }

   xl=T1;
   xh=T2;
   ans=UNUSED;
   for (j=1;j<=MAXIT;j++)
   {

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xm=0.5*(xl+xh);
(*Strain)(E,xm,Ni,Nf,S1,S10,&Ntz,&Ndz);
/**** First function evaluation of each iteration ****/
gm= *S1+xm*tp/Cs/ts;
s=sqrt(gm*gm-gl*gh);
if (s == 0.0) return ans;
xnew=xm+(xm-xl)*((gl >= gh ? 1.0 : -1.0)*gm/s);
if ((fabs(xnew-ans) <= tol) || (fabs((xnew-ans)/ans)<ptol))
{
   (*Strain)(E,ans,ni,Nf,S1,S10,&Ntz,&Ndz);
   *Nt=Ntz; *Nd=Ndz; return ans;
}
ans=xnew;
(*Strain)(E,ans,Ni,Nf,S1,S10,&Ntz,&Ndz);
/**** Second function eval of each iteration ****/
gnew= *S1+ans*tp/Cs/ts;
if (gnew == 0.0) (*Nt=Ntz; *Nd=Ndz; return ans;)
if (SIGN(gm,gnew) != gm)
{
    xl=xm;
    gl=gm;
    xh=ans;
    gh=gnew;
}
else if (SIGN(gl,gnew) != gl)
{
    xh=ans;
    gh=gnew;
}
else if (SIGN(gh,gnew) != gh)
{
    xl=ans;
    gl=gnew;
}
else printf("never get here.\n");
if ((fabs(xh-xl) <= tol) ||
    (fabs((xh-xl)/xh)<ptol))
{
   (*Strain)(E,ans,ni,Nf,S1,S10,);
   *Nt=Ntz; *Nd=Ndz; return ans;
}
printf("zriddr exceed maximum iterations.\n");
}
#undef MAXIT
#undef UNUSED
#undef NRANSI

The following routine is used to average together more than one time simulation if required. During each run, a new set of energy barriers will be generated. Both the strain and the electrical displacement will be calculated by the Averaging method and the series expansion method. The function pointer (*Strain) sets the appropriate function to use when the two different methods are used.
void average(double *E, double Tapp, double Epol, int num,
    double *Sml, double *Dm, double *Scm, double *Dcm)
{
    register int i,k,t;
    int Nf[MAXN],N0m[MAXN],N0cm[MAXN], N1[MAXN],tempN[MAXN];
    double S1[MAXT],D3[MAXT],temp,S10,T,Ti,Scm0,Nt,Nd;

    /*** Initialize variables ***/
    S1[0]=0.0; D3[0]=0.0; Scm[0]=0.0; Dcm[0]=0.0;

    /*** Initialize mean variables ***/
    for (t=0 ; t<Step ; t++) {Sml[t]=0.0; Dm[t]=0.0;}

    /*** Averaging ***/
    for (k=0 ; k<num ; k++)
    {
        /*** Generate energy barriers for each run ***/
        energy();

        /*** Initialize model to virgin state ***/
        S10=0.0; Scm0=0.0;
        for (i=0 ; i<nPHI*nPSI ; i++) N1[i]=2;
        /*** Pole model ***/
        sswitch(Epol,0.0,N1,tempN,&temp,0.0,&(Ntm[0]),&(Nd[0]));
        sswitch(0.0,0.0,tempN,N0m,&S10,0.0,&(Ntm[0]),&(Nd[0]));
        sswitchcm(Epol,0.0,N1,tempN,&temp,0.0,&(Ntm[0]),&(Nd[0]));
        sswitchcm(0.0,0.0,tempN,N0cm,&Scm0,0.0,&(Ntm[0]),&(Nd[0]));
        printf("Finish poling.\n");

        /*** Check to see if clamping exists ***/
        if (flagT==1)
        {
            /*** if stress is given, directly compute ***/
            /*** S and D from the poled initial state ***/
            for (t=1 ; t<Step ; t++)
            {
                /*** Averaging method ***/
                Strain=sswitch;
                (*Strain)(E[t],Tapp[t],N0m,Nf,&(S1[t]),S10,&Nt,&Nd);
                D3[t]=electdisp(E[t],Tapp[t],Nf);
                for (i=0 ; i<nPHI*nPSI ; i++)
                    N0m[i]=Nf[i];

                /*** Chen and Mont method ***/
                Strain=sswitchcm;
                (*Strain)(E[t],Tapp[t],N0cm,Nf,&(Scm[t]),Scm0,
                    &Nt,&Nd);
                Ntm[t]=Nt; Ndm[t]=Nd;
                Dcm[t]=Ps*Nt+macro[2]*Nt*Tapp[t]+
                       (macro[4]+macro[5]*fabs(Nt))*E[t];
                for (i=0 ; i<nPHI*nPSI ; i++)
                    N0cm[i]=Nf[i];
            }
        }
        else
        {
            Ti=0.0;
        }
    }
}
for (t=1 ; t<Step ; t++)
{
    /*** if stress not given, iteration ****/
    /*** on equilibrium by Ridder must ****/
    /*** be used for clamped cases.       ****/
    
    /*** Chen and Mont method ****/
    Strain=sswitchcm;
    T=zriddr(E[t],N0cm,Nf,Ti,&(Scm[t]),Scm0,  
        Scm[t-1],&Nt,&Nd);
    if ( (T != 0.0) || (T == -1.11e30) )
    {
        Dcm[t]=macro[2]*Nt*T+Ps*Nt+E[t]*  
            (macro[4]+macro[5]*fabs(Nt));
        for (i=0 ; i<PHI*NPSI ; i++)
            N0cm[i]=Nf[i];
        /*** Update stress ****/
        Ti=T; Ntm[t]=Nt; Ndm[t]=Nd;
    }
    else
    {
        printf("Ridder's method failed.\n");
        exit(1);
    }

    /*** Averaging Method ****/
    /*** Use equilibrium stress from last method ****/
    Strain=sswitch;
    T=zriddr(E[t],N0m,Nf,Ti,&(S1[t]),S10,S1[t-1],&Nt,&Nd);
    if ( (T != 0.0) || (T == -1.11e30) )
    {
        D3[t]=eletdisp(E[t],0.0,Nf);
        for (i=0 ; i<PHI*NPSI ; i++)
            N0m[i]=Nf[i];
        /*** Don't update stress, already did ****/
    }
    else
    {
        printf("Ridder's method failed.\n");
        exit(1);
    }
}
for (t=0 ; t<Step ; t++)
{
    Sm1[t]=Sm1[t]+S1[t]/num;
    Dm[t]=Dm[t]+D3[t]/num;
}
}

The following routine is used to write the results of the simulation to a .MAT file compliant with the Matlab 4.0 format.

void stordoub(double *arr, FILE *fp, char *pname)
{

Fmatrix head;
int mn;

head.type=1000;
head.mrows=Step; head.mcols=1;
head.imagf=0;
head.namlen=strlen(pname)+1;
fwrite(&head,sizeof(Fmatrix),1,fp);
fwrite(pname,sizeof(char),head.namlen,fp);
mn=head.mrows*head.mcols;
fwrite(arr,sizeof(double),mn,fp);
}

main()
{

    double Scm[MAXT],Dcm[MAXT],Sm1[MAXT],Dm[MAXT];
double E[MAXT],Tapp[MAXT],phi[MAXPHI],psi[MAXPSI];
double Epol,tf,Ae,w;
FILE *pinT,*pinput,*pout;
char *name;
int num;

    /*** Declare simulation parameters ***/
    double Scm[MAXT],Dcm[MAXT],Sm1[MAXT],Dm[MAXT];
    double E[MAXT],Tapp[MAXT],phi[MAXPHI],psi[MAXPSI];
    double Epol,tf,Ae,w;
    FILE *pinT,*pinput,*pout;
    char *name;
    int num;

    /*** Read in data ***/
    pinput=fopen("input.dat","r");
    pinT=fopen("Tim.dat","r");
    fscanf(pinput,"flagT=%d
 step=%d
",&flagT,&Step);
    if (flagT==1)
    {
        Step=0;
        while (!feof(pinT))
            fscanf(pinT,"%lf\n",&(Tapp[Step++]));
    }
    fscanf(pinput,"tf=%lf \nw=%lf\n",&tf,&w);
    fscanf(pinput,"nphi=%d \npsi=%d \nSc=%lf\n",&nPHI,&nPSI,&PS,&Sc);
    fscanf(pinput,"Up=%lf \nUs=%lf\n",&Up,&Us);
    fscanf(pinput,"rUp=%lf \nr Ud=%lf \nr us=%lf\n",&rUp,&rUd,&rUs,&rUs);

    /*** Read in crystallite properties ***/
    fscanf(pinput,"s11=%lf\ns12=%lf\n",&(micro[0]),&(micro[1]));
    fscanf(pinput,"s13=%lf \ns33=%lf \ns44=%lf\n",&(micro[2]),&(micro[3]),&(micro[4]));
    fscanf(pinput,"s66=%lf \n16=%lf \ne3=%lf\n",&(micro[12]),&(micro[5]),&(micro[6]));
    fscanf(pinput,"d31=%lf \nd33=%lf \nd15=%lf\n",&(micro[7]),&(micro[8]),&(micro[9]));

    /*** Read in macroscopic properties ***/
    fscanf(pinput,"si=%lf \nsn=%lf \nd=%lf\n",&(macro[0]),&(macro[1]));
    fscanf(pinput,"h=%lf \nel=%lf \nen=%lf\n",&(macro[3]),&(macro[4]),&(macro[5]));
    fscanf(pinput,"Epol=%lf \n Epot=%lf\n",&Epol,&tp);
    fscanf(pinput,"num=%d \n \ntol=%lf \ntol=%lf\n",&num,&tol,&ptol);
}
/** Read in varying parameters ***/
fscanf(pininput,"Ae=%lf \nCs=%lf \nts=%lf\n",&Ae,
 &{micro[10]},&(micro[11]));

/** Set up Simulation parameters ***/
setup(E,tf,Ae,w,phi,psi);
pack();
work();
callload();
/** Start simulation ***/
average(E,Tapp,Epol,num,Sml,Dm,Scm,Dcm);

/** Write to MAT file ***/
pout=fopen("euler.mat","w"); printf("Writing Data.\n"); name="E"; stordoub(E,pout,name);
name="T"; stordoub(Tapp,pout,name);
name="Sml"; stordoub(Sml,pout,name);
name="Dm"; stordoub(Dm,pout,name);
name="Scm"; stordoub(Scm,pout,name);
name="Dcm"; stordoub(Dcm,pout,name);
name="Ntm"; stordoub(Ntm,pout,name);
name="Ndm"; stordoub(Ndm,pout,name);
fclose(pininput);
fclose(pout);
}
Appendix C: Material Properties of PZT–5H

This appendix summarizes the important constitutive properties of the PZT–5H wafers used in all the experiments. These are 2 inch by 1 inch by 12.5 mil PZT–5H wafer manufactured by Morgan Matroc, Inc. Each of them are electroplated with nickel electrodes on both sides. All of them were poled and aged during the manufacturing process. The following properties are obtained from Reference 65.

Table c-1. Dielectric properties of PZT–5H at 1 kHz.

\[
\begin{array}{|c|c|}
\hline
\varepsilon_{33}^T / \varepsilon_o & 3400 \\
\varepsilon_{33}^S / \varepsilon_o & 1470 \\
\varepsilon_{11}^T / \varepsilon_o & 3130 \\
\varepsilon_{11}^S / \varepsilon_o & 1700 \\
\hline
\end{array}
\]

Table c-2. Elastic properties of PZT–5H. Compliances are in $10^{-12} \text{m}^2/\text{N}$, and stiffnesses are in $10^{10} \text{N/m}^2$.

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\delta_{11} & 16.5 & s_{11}^D & 14.05 & c_{11}^E & 12.6 & c_{11}^D & 13.0 \\
\delta_{33}^E & 20.7 & s_{33}^D & 8.99 & c_{33}^E & 11.7 & c_{33}^D & 15.7 \\
\delta_{44}^E & 43.5 & s_{44}^D & 23.70 & c_{44}^E & 2.30 & c_{44}^D & 4.22 \\
\delta_{66}^E & 42.6 & s_{66}^D & 42.6 & c_{66}^E & 2.35 & c_{66}^D & 2.35 \\
\delta_{12}^E & -4.78 & s_{12}^D & -7.27 & c_{12}^E & 7.95 & c_{12}^D & 8.28 \\
\delta_{13}^E & -8.45 & s_{13}^D & -3.05 & c_{13}^E & 8.41 & c_{13}^D & 7.22 \\
\hline
\end{array}
\]

Table c-3. Piezoelectric properties of PZT–5H. The units for the constants are: $d$ ($10^{-12} \text{m/V}$), $e$ ($\text{Coul/m}^2$), $g$ ($10^{-3} \text{Vm/N}$), and $h$ ($10^8 \text{V/m}$).

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
d_{31} & -274 & e_{31} & -6.55 & g_{31} & -9.11 & h_{31} & -5.05 & k_{31} & -0.388 \\
d_{33} & 593 & e_{33} & 23.3 & g_{33} & 19.7 & h_{33} & 18.0 & k_{33} & 0.752 \\
d_{15} & 741 & e_{15} & 17.0 & g_{15} & 26.8 & h_{15} & 11.3 & k_{15} & 0.675 \\
\hline
\end{array}
\]
Glossary

123-Frame: Frame of reference with the 3-axis attached to the polar axis of a crystallite.

Barium Titanate: A ferroelectric crystal or ceramic with perovskite structure. It’s Curie point is at 120°C, and has three ferroelectric phases. The first ferroelectric–ferroelectric phase transition is at 0°C, from a tetragonal structure to an orthorhombic. The second is at -90°C, from an orthorhombic to a rhombohedral.

Ceramic: A non-metallic polycrystalline solid.

Coercive field: The level of electric field required to change the remanent polarization in a ferroelectric from its saturation value to zero.

Ceramic Frame: Frame of reference fixed with the ceramic body, serves as the global reference frame.

Crystal Frame: Frame of reference fixed to a crystallite to describe the orientation.

Curie point: A temperature at which a ferroelectric undergoes a structural transition in the crystal lattice. As the ferroelectric is heated pass the Curie point, the spontaneous polarization vanishes.

Curie temperature: A temperature at which the reciprocal of the relative dielectric permittivity vanishes. This temperature is always less than or equal to the Curie point.

Direct Averaging Method: Method to calculate macroscopic ceramic responses from the crystallite responses by directly average the vector and tensor component of all the crystallite responses.

Domains: Regions in a ferroelectric which has uniform spontaneous polarization.

Doping: A process which substitute a type of ion in the lattice by another type that has different valence in order to modify the material behavior. In PZT, soft dopants like La$^{3+}$ and Nb$^{5+}$ creates Pb vacancies in the lattice and donor impurities to increase domain wall mobility and resistivity, causing increases in loss and coupling factors. On the other hand, hard dopants like Fe$^{3+}$ and K$^{+}$ creates O$^{2+}$ vacancies and acceptor impurities to inhibit domain wall motion, causing the opposite effects of the soft dopants. See also Lead Zirconate Titanate.

Electrostrictives: Nonpolar materials that produce strain proportional to the quadratic of the applied electric field. The sign of the produced strain does not reverse with the applied field.

Effective Poling Field: The field level used to initialize the model that will give a roughly equivalent material states of a well-aged ceramic.
**Equilibrium Constraint Method**: Method used to evaluate the clamping stresses in the sandwich structures that directly imposes the equilibrium of a typical section of the sandwich structure through an iterative scheme.

**Euler Angles**: A set of three angles that complete describes the orientation of a rigid body in three-dimensional space.

**Ferroelectrics**: A polar material which is subclass of pyroelectrics. The direction spontaneous polarization can be changed by an electric field.

**First order transition**: A phase transition which the spontaneous polarization of the ferroelectric vanishes abruptly with a discontinuity at the Curie point as it is heated or cooled.

**KDP**: See *Potassium Dihydrogen Phosphate*.

**Lead Zirconate Titanate (PZT)**: A ferroelectric ceramic composed of lead titanate (PbTiO₃) and zirconium titanate (ZrTiO₃) with a distorted perovskite structure. Compositions of commercial products usually are doped with small amount of other metal ions such as barium or niobium to create "hard" and "soft" variants. Hard variants generally have less mobile domain walls and smaller electromechanical coupling, whereas the soft variants are the opposite. See also *Doping*.

**Paraelectric**: A material which has a relative dielectric permittivity that follows the Curie-Weiss Law and the material exhibits no spontaneous polarization.

**Perovskite**: A common name for calcium titanate, also used to name a cubic crystal structure with formula ABO₃. A is mono- or divalent metal ion at the corners of the unit cell. B is tetra- or pentavalent metal ion in the body center and the oxygen ions are on the face centers.

**Phenomenology**: Method of representing of material behaviors in terms of macroscopic properties that are directly measurable. Microscopic details of the material is usually neglected.

**Piezoelectric**: Polar materials which produce a proportional surface charges to the applied stress. Strictly speaking, piezoelectricity implies linearity between charge and stress.

**Polarization Reversal**: A procedure which the remanent polarization of a ferroelectric is reversed in direction by an external electric field. See also *Remanent polarization*.

**Poling**: A process which a dc electric field larger than the coercive field is applied to a multi-domain ferroelectric to create a net remanent polarization. See also *Remanent polarization*.

**Potassium Dihydrogen Phosphate (KDP)**: A ferroelectric with formula KH₂PO₄. Ferroelectricity of KDP is due to the hydrogen bonds in the crystal structure. KDP has a paraelectric phase which possess piezoelectricity. It’s Curie point is at -150°C.
**Previous Time Step Method:** Method used to evaluate the clamping stresses in the sandwich structures that uses the resultant strain level from the previous time step.

**Pyroelectrics:** A polar material which possess spontaneous polarization that can be changed when uniformly heated or cooled. The direction of the spontaneous polarization, however, cannot be changed by an external electric field. See also *Spontaneous polarization*.

**PZF:** See *Lead Zirconate Titanate*

**Remanent polarization:** Polarization remains in a ferroelectric after electric field is removed. In a single domain, remanent polarization equals to the spontaneous polarization. See also *Spontaneous polarization*.

**Resonant Frequency Method:** Method developed to measure the linear material properties of piezoelectric materials.

**Second order transition:** A phase transition which the spontaneous polarization of the ferroelectric vanishes continuously as it is heated or cooled pass the Curie point.

**Series Expansion Method:** Method to calculate macroscopic ceramic responses from the crystallite polarization behavior using polynomial series expansion of macroscopic quantities.

**Spontaneous polarization:** Polarization in one single domain in a ferroelectric when no external electric field is applied.
References


