Chapter 1

Introduction

1.1. Piezoelectricity

The phenomenon of piezoelectricity was discovered by Jacques and Pierre Curie brothers in 1880 [1]. Piezoelectric materials are the class of dielectric materials that can be polarized due to an applied electric field, also by application of a mechanical stress. Thus, piezoelectricity is said to be an interaction between electrical and mechanical systems (Figure 1.1).

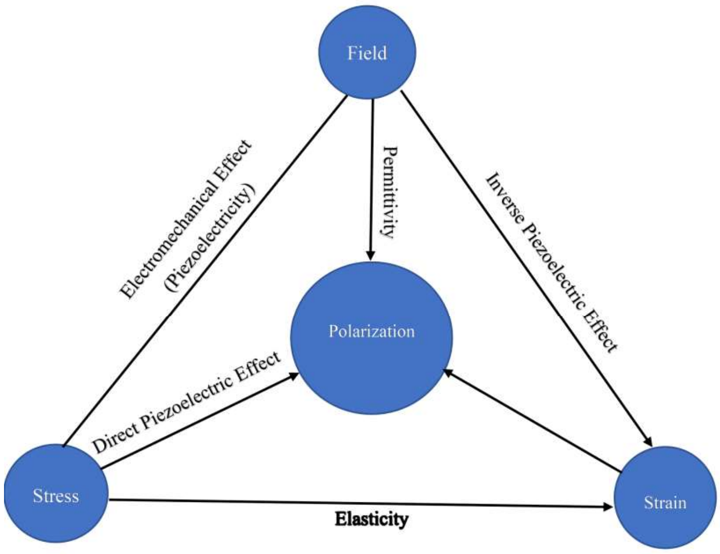


Figure 1.1 Piezoelectricity: An intermingling of elastic and electric phenomenon.

Further, piezoelectric materials can be subdivided into two categories, i.e., polar and non-polar piezoelectric materials. Polar piezoelectric materials are those that possess a net dipole moment and non-polar piezoelectric materials are those that possess a null total moment. In non-polar piezoelectric materials, the dipole moments of discrete domains are aligned in different directions which when summed over the entire region give zero net dipole moment.

The development of an electric charge upon the application of a mechanical stress is termed as direct piezoelectric effect and represented mathematically as [2]

$$P_i = d_{ijk}\sigma_{jk} \tag{1.1}$$

where P_i is generated fixed charge density (charge per unit area), d_{ijk} are the piezoelectric coupling coefficient components, and σ_{jk} are the applied mechanical stress components. Similarly, the development of a mechanical strain upon the application of an electric field is termed as indirect piezoelectric effect and represented mathematically as

$$\varepsilon_{ij} = d_{ijk}E_k \tag{1.2}$$

where ε_{ij} are the strain tensor and E_k are the electric field vector. In both cases, the piezoelectric coupling coefficients d_{ijk} remains numerically identical.

The direct and converse piezoelectric effect is strongly linked to the crystal symmetry. Piezoelectricity phenomenon is limited to 20 of the 32 crystal classes known as point groups. There is a unique common feature among crystals which exhibit piezoelectricity, i.e., the absence of a centre of symmetry within the crystal. This absence of symmetry leads to a displacement between anions and cations when exposed to change in the dimension due to application of external stress. This results in polarization, i.e., the one-way direction of the charge vector. Most of the important piezoelectric materials are also ferroelectric. Ferroelectric materials are a class of materials which have the ability to transform to high symmetry non-piezoelectric phase at higher temperatures. The critical transformation temperature is known as the Curie temperature. The Curie temperature is the measure of absolute maximum use temperature for any piezoelectric material, above which it loses its piezoelectric characteristics.

In polycrystalline piezoelectric materials the crystal axes of the grains are randomly oriented, hence they exhibit net zero polarization. Piezoelectric polycrystalline ceramics were first discovered in the 1940s, followed by development of the poling process. In the poling process, the randomly oriented crystal axes are suitably aligned by applying a strong electric field at an elevated temperature. These two discoveries led to the synthesis of materials having better and more stable piezoelectric properties. Introduced in the year 1954, lead zirconate titanate (PZT) has become the most widely used piezoceramic till date. Due to anisotropy, the electromechanical properties of piezoelectric materials show a huge direction dependence for electrical-mechanical excitations. Hence, a systematic tabulation of their directional properties becomes of utmost importance; for using such materials in various sensing or actuating applications. A well accepted practice is to assign numerals to the axes: 1 corresponds to x-axis; 2 corresponds to y-axis and 3 corresponds to z-axis. The direction of the poling field is identified as one of the axes in operation; usually it is taken as 3. A poling field is applied in such a way that the material exhibits piezoelectric responses in either one direction or combination of two or three directions.

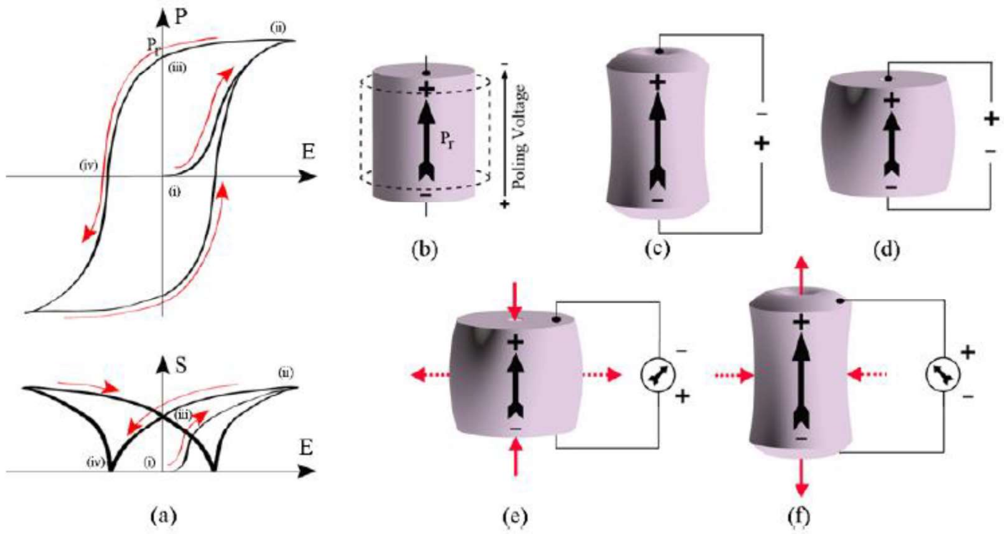


Figure 1.2 Piezoelectric materials in sensing and actuating applications; **(a)** P-E hysteresis plot (top) and S-E plot (bottom); **(b)** The piezoelectric material before and after poling; **(c)** Change in dimension when applied voltage has polarity similar to that of poling voltage; **(d)** Change in dimension when the applied voltage has polarity opposite to that of poling voltage; **(e)** The voltage generated equivalent to poling voltage when compressive force is applied in poling direction; **(f)** The voltage generated equivalent to poling voltage when tensile force is applied in poling direction. *Reference:* [3]

The poling process permanently changes the dimensions of a piezoelectric material. As illustrated in Fig. 1.2 (b), it is evident that the dimension between poling electrodes increases while the dimension parallel to the electrode decreases. After the completion of the poling process, any voltage lower than poling voltage is capable of changing the dimensions of the piezoelectric materials so long as the voltage is applied. An applied voltage with the same polarity as the poling voltage causes some additional expansion along the poling axis and contraction perpendicular to the poling axis as illustrated in Fig.

1.2 (c). One can also observe this phenomenon from P-E and S-E plots of Fig 1.2 (a). When subjected to a poling field, *E,* the polarization and mechanical strain curves follow the path shown by (i)-(ii) on P-E and S-E plots, respectively. After the removal of the poling field, the behaviour curves follow the path (ii)-(iii) and it can be noticed from the figure that the piezoelectric material retains some remanent polarization, P_r . Because of that remnant polarization the material experiences a permanent strain or change in change in dimensions. The poling process shifts the working point from (i) to (iii) now from an operational point of view. It implies that whenever a voltage of the same polarity as of poling is applied along the poling axis; the P-E and S-E plots will follow the curve (iii)-(ii) and hence a positive strain will be developed. Similarly, when a voltage with the polarity opposite to that of poling is applied along the poling axis; the P-E and S-E plots will follow the path (iii)-(iv), resulting in a negative strain. However, in both the cases, the piezoelectric material returns to its original poled dimensions (working point (iii)) when the applied voltage is removed from the electrodes.

1.2. Piezoelectric Effect- Basic Mathematical Formulation

This section presents an overview of the basic mathematical relations that describes the direct and converse effects exhibited by a piezoelectric material. The linear theory of piezoelectricity [3] suggests that the piezoelectric materials exhibit a linear profile at a low level of applied external electrical fields and mechanical stresses. For the range of mechanical stresses and electric fields used in this work, the piezoelectric materials exhibit linearity. The mathematical relations that describe the coupling between stress σ_{ij}, strain ε_{kl}, electric field E_i and dielectric constant D_i are given as [4]

$$\varepsilon_{ij} = s^E_{ijkl}\sigma_{kl} + d_{ijk}E_k \tag{1.3}$$

$$D_i = d_{ijk}\sigma_{jk} + \kappa_{ij}^{\sigma}E_j \tag{1.4}$$

where the dielectric displacement, D_i is represented by the sum $\kappa_0 E_i + P_i$. Here, κ_{ij} and s_{ijkl} are the permittivity tensor and elastic compliance tensor, and κ_0 is the dielectric constant of free space. Superscripts σ and E added to κ_{ij} and s_{ijkl} indicates that these constants are measured under conditions of constant stress and constant electric field, respectively.

Alternatively, these constitutive relations can also be expressed as follows:

$$\sigma_{ij} = c_{ijkl}^{E}\varepsilon_{kl} - e_{kij}E_k \tag{1.5}$$

$$D_i = e_{ikl}\varepsilon_{kl} + \kappa_{ij}^{\varepsilon}E_j \tag{1.6}$$

where the piezoelectric constants e_{ijk} are related to the piezoelectric constants d_{imn} and the elastic stiffness constants c_{ijkl}^{E} by the following expression: $e_{ijk} = d_{imn}c_{mnjk}^{E}$. An alternation notation of abbreviated subscripts that reduces the three subscripts of the piezoelectric constants and the four subscripts of the elastic constants into two subscripts is known as "Voigt notations". The relationship of full subscripts with abbreviated subscripts for piezoelectric and elastic constants are outlined in the IEEE standard on Piezoelectricity [4].

Further, the strain and electric field given in Eqns. (1.3) and (1.4) are derived from the mechanical displacement and electric potential and represented as

$$\varepsilon_{ij} = \frac{1}{2}\left(u_{i,j} + u_{j,i}\right) \tag{1.7}$$

$$E_i = -\varphi_{,i}\ . \tag{1.8}$$

Eqns. (1.3) to (1.6) must be supplemented with Eqns. (1.9) and (1.10) to account for conditions of elastic equilibrium and the electrostatic equilibrium in the absence of body forces and free electric charge. These equations are expressed as

$$\sigma_{ij} = 0 \tag{1.9}$$

$$D_{i,i} = 0 \, . \tag{1.10}$$

The letter suffix used with each term is with respect to Einstein summation convention [5]. According to the convention, when a letter suffix occurs twice in the same term, summation with respect to that suffix is to be automatically understood. In Eqn. (1.5), i, j are free suffixes and k, l are called dummy suffixes. The free suffix must be the same in all terms on both sides of the equations; while the dummy suffixes must occur as pairs in each term. In the present thesis, the range of values of all letter suffixes is *1, 2, 3* unless some other range is specified (for example, see Appendix A).

Piezoelectric materials have a wide range of applications in hydro, electro-acoustic, electro-optics, communications and measurement techniques. They are also used for control purposes in lightweight smart structures. These materials have huge potential for other advanced engineering applications, e.g., space explorations, remote control of spacecraft etc.

1.3. Piezoelectric Composites

1.3.1. Background

Many piezoelectric composite materials have been developed over the past two decades with effective properties tailored for specific applications. Piezocomposites are fabricated by combining two or more distinct constituents. These materials can take the advantages of each of the constituents to provide superior electromechanical coupling characteristics when compared with their monolithic counterparts. Piezocomposites have been developed in multiple forms that include polymer filled secondary-phase piezoelectric inclusions in a solid piezoelectric ceramic matrix and secondary-phase piezoelectric ceramic inclusions embedded in a polymer matrix. These secondary-phase piezoelectric inclusions could be of varied geometries, i.e., continuous fibers, short fibers, dispersed particles, or voids. Piezocomposites were originally developed for underwater hydrophone applications in the low-frequency range, but later been extended to many other applications, e.g., underwater acoustic and medical ultrasonic imaging applications, aerospace etc. Hence, piezoelectric composites constitute an important branch of the recent emerging technologies of modern engineering materials.

Structural composite materials are formulated to optimize mechanical properties while piezoelectric composite materials are designed to maximize their coupled field behaviour. Hence, the determining factor for designing a piezoelectric composite, whether as an actuator or a sensor, is to ensure the maximum efficiency in electromechanical energy conversion [6]. Like any composite material, the properties and behaviour of piezoelectric composites are highly dependent on the properties of the constituent phases as well as local arrangements of these different phases. However, the material exhibits anisotropy due to introduction of inclusions or voids into the base media and makes analysis complicated. Therefore, it is necessary to examine the electroelastic responses of such piezocomposites from a micromechanics point of view so that the influence of material parameters on the overall properties can be understood thoroughly.

1.3.2. Connectivity Patterns

The arrangement of the different phases comprising a composite plays an important role in determining those field patterns that dictate electromechanical properties of a composite. The concept of connectivity that was first developed by Newnham *et. al.* [7-8]. It is a convenient tool to describe the continuity of each individual phase in three dimensional spaces. For a two-phase system, i.e., diphasic system, 10 such connectivity patterns exist. Each phase could be continuous in 0, 1, 2, or 3 dimensions as illustrated in

Fig. 1.3. The widely accepted nomenclature to describe connectivity of such composites is given by closed bracketed numerals, e.g., (0-0), (0-1), (0-2), (0-3), (1-1), (1-2), (2,2), (1-3), (2-3), and (3-3). In the above notation, the first digit within parenthesis refers to the number of dimensions in which the first phase (generally piezoelectrically active) is continuous; and the second digit refers to the number of dimensions in which the second phase (often piezoelectrically inactive) is continuous. Based on these connectivity patterns, an array of piezoelectric composites has been developed as shown in Fig. 1.4.

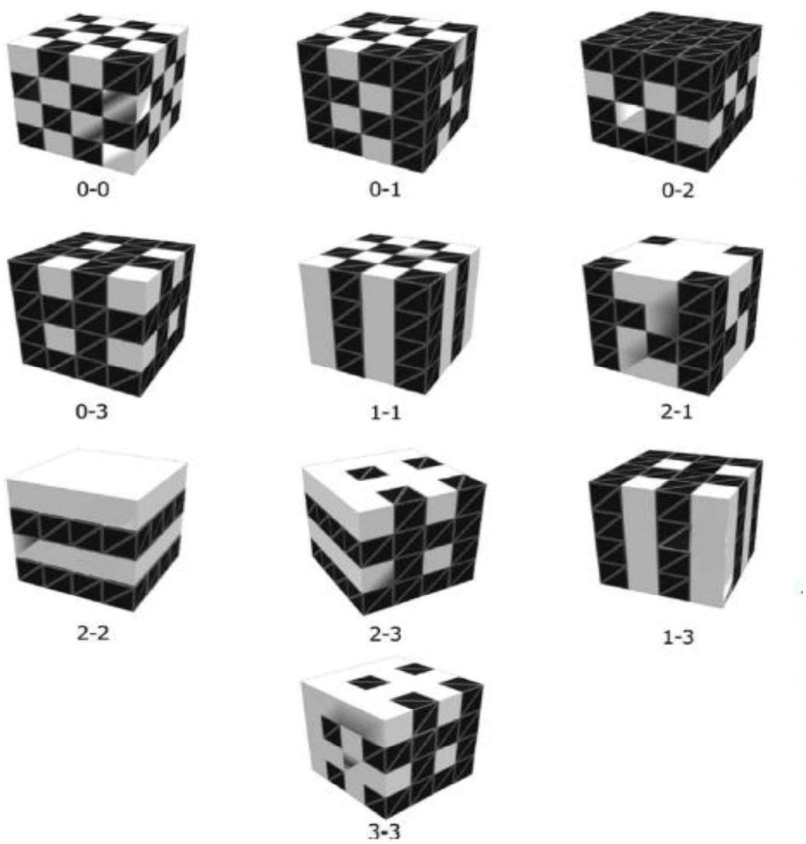


Figure 1.3 Connectivity families for diphasic composites. The total number of connectivity patterns arising out of 10 families depicted is 16 due to permutations of order involved in families; {0-2}, {0-3}, {1-0}, {1-3}, {2-1}, {2-3}. *Reference:* [9]

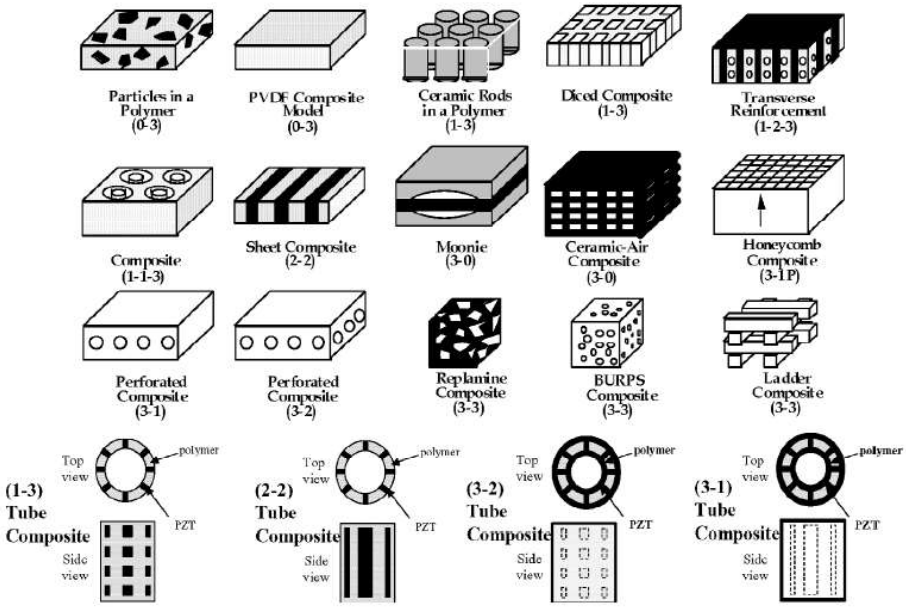


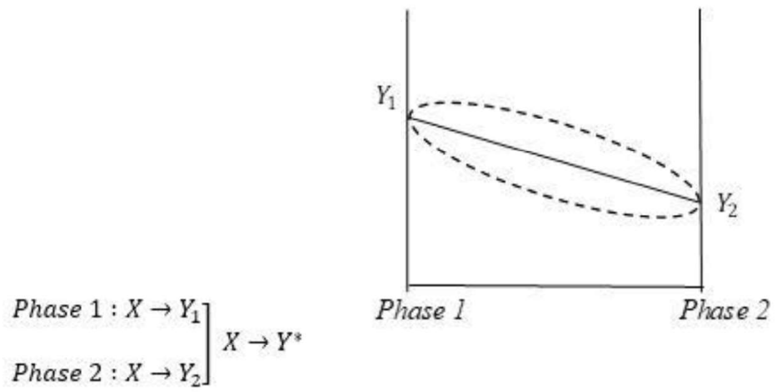
Figure 1.4 Schematic diagram showing composites with various connectivity patterns realized over the past 40 years. *Reference:* [9]

During the course of time, few modifications to the list also occurred. Pilgrim *et. al.* [10] suggested six additional connectivity patterns, raising the total number of connectivity patterns to 16 for a diphasic composite. The additional connectivity patterns arise out of the convention that two composites of the same phases and connectivity could differ when their connectivity order is interchanged. To further elaborate this, a composite formed from piezoelectric rods embedded in polymer matrix shows a different piezoelectric response than a composite formed from piezoelectric monolith with polymer filled channels. The former composite would be classified as (1-3), while the latter would be classified as (3-1). With the consideration of additional connectivity patterns, the extended nomenclature list becomes; (0-0), (1-0), (0,1), (0-2), (2-0), (0-3), (3-0), (1-1), (1-2), (2-1), (1-3), (3-1), (2-2), (1-3), (3-2), (3-3). It should be worth noting that these 6 additional connectivity patterns don't interfere with the representation of 10 connectivity pattern families. In these representations, a given family is denoted by curly brackets, for instance, {3-0}. This suggests that the family includes the patterns (0-3) as well as (3-0) with the active phase's connectivity written first. In other words, the extension of the nomenclature only renders connectivity patterns in the connectivity families, allowing the observer to include all the permutations involved.

1.3.3 Composite Effects

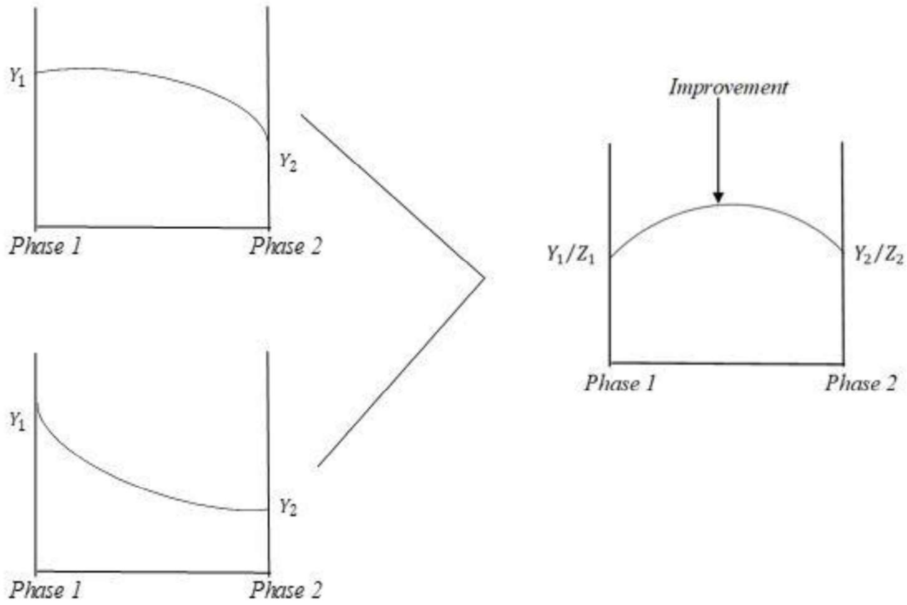
Composite effects can be broadly classified into three categories, i.e., the sum effect, the combination effect and the product effect, as depicted in Fig. 1.5. Suppose for a diaphasic system, a composite function converts an input parameter X to an output parameter Y. Y_1 and Y_2 are the two distinct values for outputs from Phase 1 and 2, respectively, responding to the same input X. Y^* is the value of output of the composite and could be any value intermediate in between individual phase output values, i.e., Y_1 and Y_2.

(a) Sum effect:



(b) Combination effect:

$$\left.\begin{array}{l} Phase\ 1: X \rightarrow Y_1/Z_1 \\ Phase\ 2: X \rightarrow Y_2/Z_2 \end{array}\right] X \rightarrow (Y/Z)^*$$



(c) Combination effect:

$$\left.\begin{array}{l} Phase\ 1: X \rightarrow Y \\ Phase\ 2: Y \rightarrow Z \end{array}\right] X \rightarrow Z \quad New\ function$$

Figure 1.5 Composite effects: **(a)** sum effect; **(b)** combination effect; **(c)** product effect.

Reference: [11]

Figure 1.5 (a) illustrates the variation of Y^* with change in volume fraction of Phase 2 for a case $Y_1 > Y_2$. This variation plot may exhibit a concave or a convex shape, but its average value will lie within the bounds of Y_1 and Y_2. And, this characteristic is termed as a "sum effect".

In certain cases, the average value of output Y^* of a composite seems to exceed the bounds of individual phase output values, Y_1 and Y_2. This enhancement of output refers to an effect that is characterized by the ratio Y/Z, and hence depends on parameters Y and Z. Now, if Y and Z both follow the concave and convex type sum effects, respectively, at a time, the combination value Y/Z will attain a maximum at some intermediate ratio of individual phases. This characteristic is well illustrated in Fig. 1.5 (b), and is named as a "combination effect".

Fig 1.5 (c) represents the formulation for a "product effect". Phase 1 shows an output Y as a response to an input X and subsequently Phase 2 shows an output Z as a response to an input Y. An output Z is expected as a response to an input X for the composite. Hence with these operations, a totally new function is generated for the composite structure. This characteristic is termed as "product effect".

1.4. Motivation

The previous sections discuss the phenomenon of piezoelectricity, the mathematical formulation of piezoelectric responses, background of piezoelectric composites, connectivity patterns and combination effects. From the above discussion, it can be concluded that the material properties of constituents, connectivity pattern and the geometry of the inclusion (or inhomogeneity) plays a significant role in determining the effective properties of the piezocomposites.

The main motivation to carry out this research work is to study the coupled field problems of the piezoelectric composites by developing a rigorous mathematical framework that is capable of solving various inclusion (and/or inhomogeneity) problems related to such composites. The overall properties of the piezocomposites depend on interaction between its constitutive phases and the geometry of the reinforcement. Different shapes of inclusions induce different internal strain and electric fields, and then these induced fields result in the different effective piezoelectric tensors. Also, the effective dielectric (or elastic) response may be affected by the elastic (or dielectric) properties of the composites through the piezoelectric properties, which induce the interactions of the local strain and electric fields. The interaction between these coupled fields is one of the key determinants of the overall properties of the piezocomposites. With mathematical (analytical and/or numerical) formulation of the inclusion and inhomogeneity problems, substantial progress can be made towards understanding the complicated micro-structural level fields and interaction among them. Also, this would help to develop a more generalized formula for determining the effective properties of the piezoelectric composite.

1.5 Summary

In the first section of this chapter, the phenomenon of piezoelectricity and its origin were discussed; the next section presented the mathematical formulation of piezoelectric responses (direct and converse effects). In the third section, the background of piezoelectric composites had been discussed at great length. It was followed by the sub-sections on the connectivity patterns of the fiber and matrix materials and combination effects arises out of such combination of fiber and matrix phases. In the fourth section, the main motivation behind carrying out the present research had been discussed in detail.