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Fundamentals of Piezoelectricity

1.1 Introduction

In 1880, Pierre Curie and Jacques Curie discovered the (direct) piezoelectric effect in quartz (SiO_2) and other single crystals, which generates an electric charge proportional to a mechanical stress. The converse piezoelectric effect, a geometric strain proportional to an applied voltage, was also soon realized. Since then, quartz has been one of the most well-known and widely used piezoelectric materials. Many decades later, polycrystalline piezoelectric ceramics (oxides) have been discovered. The first one is $BaTiO_3$ that was discovered during the World War II, which was used as dielectric materials for solid condensers at first [1]. In 1947, Roberts found that $BaTiO_3$ ceramics (polycrystals) showed good piezoelectricity, about 100 times higher than that of quartz, after they were poled under a high voltage [2]. Since then, $BaTiO_3$ ceramics have been widely applied to transducers, sensors, and filters, particularly in Japan. In 1952, Shirane et al., reported that solid solutions can be formed between $PbTiO_3$ and $PbZrO_3$ [3, 4]. One year later, ferroelectricity and antiferroelectricity were found in the solid solutions [5]. In 1954, Jaffe et al. studied the piezoelectric properties of $PbTiO_3$–$PbZrO_3$ solid solution ceramics, and found that its piezoelectric constants were twice as high as that of $BaTiO_3$, and its Curie temperature (above which the piezoelectricity disappears) was over 300 °C [6]. Now, the $PbTiO_3$–$PbZrO_3$ solid solutions, abbreviated as PZT, are the most widely used piezoelectric ceramics [7–10]. The PZT ceramics show greatly enhanced piezoelectric and dielectric properties when the Zr/Ti ratio is close to 52/48, where exists a morphotropic phase boundary (MPB) separating the rhombohedral and tetragonal regions [7]. It is generally understood that the piezoelectricity enhancement stems from the effect of phase coexistence enabled by the existence of MPB.

Despite the facts that $BaTiO_3$ is lead-free and was also discovered before PZT, the markets of piezoceramic applications have been dominated by PZT-based ceramics mainly because of its following advantages compared with $BaTiO_3$: (i) excellent and adjustable piezoelectric properties, (ii) relatively high Curie temperature, and (iii) relatively low sintering temperature. Recently, environmental protection has become a major global concern, and environmental-friendly materials and technology are one of the main tasks to be resolved in this new century. The manufacturing,

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handling, and disposal of PZT ceramics, which contain >60 wt% of lead, pose harmful influences on the workers' safety and soil environment as well as water supply. That is why many countries have incentivized the development of lead-free piezoelectric materials [11–18].

For the R&D of lead-free piezoelectric materials, it is very important to get a full understanding of piezoelectric principles and the piezoelectric mechanisms of existing piezoelectric materials, especially PZT ceramics. However, because PZT ceramics have many important applications, and in some sense, its application research has moved faster compared with the fundamental research on its piezoelectric mechanism, there are still a lot of things remaining very unclear. For example, the phase diagram of PZT around the MPB has been renewed even after half a century passed since the discovery of PZT [19–21], and rigorous descriptions still lack for unambiguous understanding of the MPB's contribution to piezoelectricity. The fundamental structure–property mechanisms revealed in lead-containing piezoelectric materials can be also operational in lead-free systems and at a minimum, should be considered as starting guidelines for the development of lead-free piezoelectrics from the aspects of composition modification, microstructure tailoring, property characterizations, device applications, etc.

1.2 Piezoelectric Effects and Related Equations

The piezoelectric effect or piezoelectricity is the generation of electric charges on the surface of certain non-conducting materials in response to applied mechanical stress, or conversely, the generation of a mechanical strain in such materials when they are subjected to an electric field, as schematically shown in Figure 1.1 [17]. The piezoelectric effect is a reversible process, so the materials exhibiting the direct

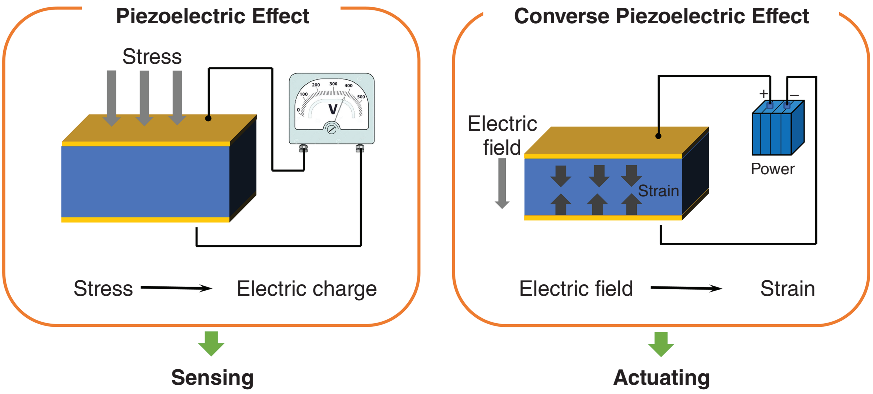

Figure 1.1 (a) The direct piezoelectric effect provides an electric charge upon application of a mechanical stress, whereas (b) the converse piezoelectric effect describes the situation where strain develops under an applied electric field. Source: Reproduced with permission from Roedel and Li [17]. Copyright 2018, Cambridge University Press.

piezoelectric effect also exhibit the converse piezoelectric effect. As such, piezoelectricity is referred to as both direct and converse effects, even though the word "piezoelectricity" often leads us to the meaning of the direct piezoelectric effect of the internal generation of electrical charges resulting from an applied mechanical force.

In a narrow sense, piezoelectricity can be understood as a linear electromechanical interaction between the mechanical and the electrical states. The constant for such a linearly proportional relation is defined as the piezoelectric coefficient d, which is a third-rank tensor coupling the first-rank tensor or vector (electric displacement or field) and the second-rank tensor (stress or strain). Hence, the piezoelectric equations may be written in the following form ($i, j, k = 1, 2, 3$) [22]

$$D_k = d_{kij} T_{ij} \tag{1.1}$$

$$S_{ij} = d_{kij}{}^{*} E_k \tag{1.2}$$

where D_i is electric displacement (C/m^2), E_i is electric field component (V/m), S_{ij} is strain component, T_{ij} is stress component (N/m^2), and d_{kij} or $d_{kij}{}^{*}$ is component of the piezoelectric charge or strain constant. It should be noted that the subscripts of piezoelectric constant are commonly expressed using the reduced Voigt matrix notation d_{km}, where k denotes the component of electric displacement D or field E in the Cartesian reference frame (x_1, x_2, x_3), and the index $m = 1, \ldots, 6$ is used to define the mechanical stress or strain. In this case, $m = 1$, 2, and 3 correspond to the normal stresses along the x_1, x_2, and x_3 axes, respectively, whereas $m = 4$, 5, and 6 stand for the shear stresses T_{23}, T_{13}, and T_{12}, respectively. Both d and d^* are called the piezoelectric constant or coefficient, but they have different units, which are pC/N and pm/V (here, p stands for 10^{-9}), respectively. It follows from thermodynamic considerations that $d_{km} = d_{km}{}^{*}$, namely, the coefficients that connect the field and strain are equal to those connecting the stress and the polarization.

In addition to the piezoelectric charge or strain constant, other forms of piezoelectric constants are also used in specialized design cases. Totally, there are four piezoelectric constants including the abovementioned piezoelectric charge or strain coefficient d, which are listed in Table 1.1 with their names and definitions [22]. These piezoelectric constants are defined as partial derivatives evaluated at constant stress (subscript T), constant electrical field (subscript E), constant electrical displacement (subscript D), or constant strain (subscript S). These conditions can be regarded as "mechanically free," "short circuit," "open circuit," and "mechanically clamped," respectively.

1.3 Ferroelectric Properties and Its Contribution to Piezoelectricity

Since most high-performance piezoelectric materials are also ferroelectric materials, it is necessary to review ferroelectric properties and their contribution to piezoelectricity [23–28]. Ferroelectricity is a character of certain materials that have a spontaneous electric polarization that can be reversed by the application of an external electric field. As illustrated in Figure 1.2, dielectrics are the big family

Table 1.1 Piezoelectric constants.

Symbol	Name	Definition
d	Piezoelectric charge coefficient or piezoelectric strain coefficient	$d_{ij} = \left(\frac{\partial D_i}{\partial T_j}\right)_E = \left(\frac{\partial S_j}{\partial E_i}\right)_T$
g	Piezoelectric voltage coefficient (voltage output constant)	$g_{ij} = -\left(\frac{\partial E_i}{\partial T_j}\right)_D = \left(\frac{\partial S_j}{\partial D_i}\right)_T$
e	Piezoelectric stress coefficient	$e_{ij} = -\left(\frac{\partial T_j}{\partial E_i}\right)_S = \left(\frac{\partial D_i}{\partial S_j}\right)_E$
h	Piezoelectric stiffness coefficient	$h_{ij} = -\left(\frac{\partial E_i}{\partial S_j}\right)_D - \left(\frac{\partial T_j}{\partial D_i}\right)_S$

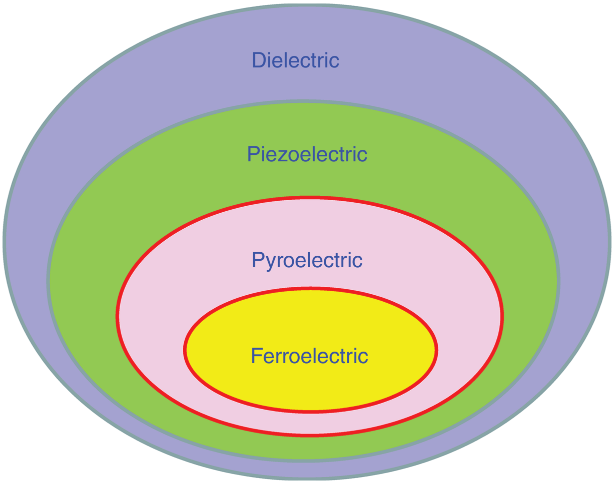

Figure 1.2 The relationship among dielectric, piezoelectric, pyroelectric, and ferroelectric materials.

with the core subset being ferroelectrics. Dielectric materials are basically electrical insulators, which become polarized by the peripheral application of electrical field when placed across the plates of a capacitor. Piezoelectric materials belong to the dielectric group, but a stress can create a net separation of positive and negative charges in a piezoelectric crystal that has a non-centrosymmetric crystal structure. Pyroelectrics are those materials with the ability to generate a temporary voltage when they are heated or cooled, since the polarization magnitude in a pyroelectric crystal can be thermally changed by the temperature change. By comparison, for a piezoelectric crystal, it is the mechanical stimuli resulting in the polarization change and as a consequence, charges build up at its surfaces. Ferroelectrics are an experimental subset of pyroelectric materials. All ferroelectric materials are pyroelectrics, and all pyroelectrics are piezoelectric; however, not all piezoelectric materials are pyroelectric and not all pyroelectrics are ferroelectric. It is known that crystal symmetry governs the aforementioned categorization. All crystalline substances belong to one of the 32 crystallographic point groups. There are 20 piezoelectric point groups and 10 ferroelectric point groups.

The direction of electric dipoles in both piezoelectric and pyroelectric (but not ferroelectric) materials cannot be changed, whereas it can be reversed by an electric field for ferroelectric materials. Therefore, the distinguishing feature of ferroelectrics is that the spontaneous polarization can be reversed by a sufficiently high applied electric field along the opposite direction. Furthermore, the polarization is dependent not only on the electric field but also on its history that the material has experienced, thereby yielding a hysteresis *P*–*E* (polarization–electric field) loop, as shown in Figure 1.3. Starting from point A, the polarization initially increases slowly with E-field, but turns to a sharp rise when the applied field is sufficiently high. Then, after a long and slow stage, the polarization reaches a saturation level (saturation polarization, P_s). The P_s is normally estimated by intersecting the polarization axis with the saturated linear part. The polarization does not go back to the starting point after the removal of E-field but instead results into non-zero values, which is defined as the remnant polarization, P_r. In order to reach a zero polarization state, an E-field applied along the opposite direction is required. This E-field is named as the coercive field, E_C, which stands for the magnitude of the applied electric field to reverse the direction of ferroelectric polarization.

The appearance of such a *P*–*E* loop is an important criterion to distinguish whether a material is ferroelectric or not. Ferroelectric materials display such a hysteretic behavior as a result of the response of electric domains to electric field, analogous to that of magnetic domains of a ferromagnetic material against a magnetic field. It should be emphasized that a polar material may be piezo-/pyro-electric but not ferroelectric if the direction of its dipoles is not switchable even under exceedingly high external electrical fields. For example, single crystalline quartz is a conventional piezoelectric material, but has no ferroelectric properties. Similarly, ZnO is a piezoelectric but non-ferroelectric material in general.

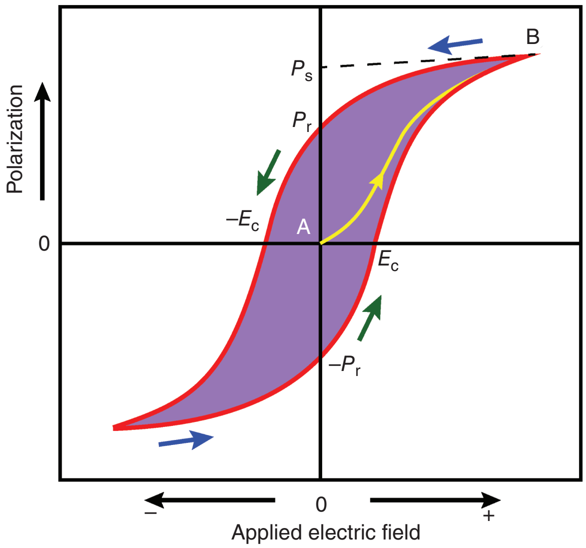

Figure 1.3 Polarization vs. electric field hysteresis loop in ferroelectric materials.

Once a ferroelectric crystal is cooled across the Curie temperature, a polarization develops. The ferroelectric phase transition is a structural phase transition, during which the displacements of ions produce lattice distortions and change the symmetry of the crystal. The magnitude of the ion displacements along certain crystallographic directions in the materials is specific to a given crystal structure and composition. If the polarization develops uniformly throughout the whole crystal, a depolarizing electric field will be produced. To minimize the electrostatic energy associated with this field, the crystal often splits into regions, called *domains*; a region in which the polarization is uniform is called a domain. The regions between two adjacent domains are called domain walls. Their thickness is typically of the order of 10–100 Å. Domain represents a region within a ferroelectric material in which the direction of polarization is uniform. The saturation polarization, P_s, corresponds to the total polarization at an extreme state where (almost) all domains are aligned along the direction of applied electric field. Some of these domains stay at the same direction even after the removal of electric field, resulting in the remnant polarization. It can be readily envisaged that a ferroelectric material at a state with remnant polarization can be used a piezoelectric material, since it can generate electric charges when subjected to mechanical stress. In other words, if a ferroelectric material, at least polycrystalline bulk materials should show no piezoelectric response if it has not been subjected to an electric field. This is because the charges will be canceled collectively if the domains are randomly distributed along different directions, resulting in zero change when the whole material receives mechanical deformation. As such, piezoelectricity can be regarded as one of the functionalities of ferroelectric materials, and in general, ferroelectric materials need to be poled before they can be used as piezoelectric materials. Therefore, electrical poling is an indispensable process for ferroelectric piezoelectric materials. During poling, a strong electric field is applied across ferroelectric materials and consequently, a majority of the domains switch their pristine polarization and become aligned along the electric field direction. Figure 1.4 schematically shows the poling process. The virgin materials are subjected to an electric field, which should be sufficiently higher

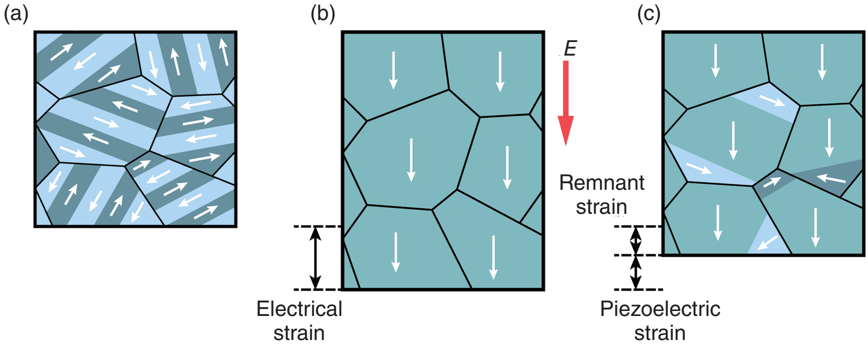

Figure 1.4 The schematic illustrations showing the alignment of ferroelectric domain and macroscopic strains when a ferroelectric material is subjected to a poling treatment under an electric field. (a) Virgin state. (b) Saturation state. (c) Remnant state.

than the coercive field (E_C), so that the domains can be re-orientated almost along the same direction. As shown in Figure 1.4b, the poling process is accompanied with an expansion of the poled materials or tensile strains, which is basically consistent with the converse piezoelectric phenomenon. As shown in Figure 1.4c, although most domains are kept along the poling direction, part of them revert back or change their orientations after the removal of the poling electrical field in order to reduce the mechanical strains. After the poling treatment, the material possesses a macroscopic polarization, which is equal to the remnant polarization (P_r) in the P–E loop shown earlier. Therefore, the poling process is very important for piezoelectric materials. Even for the same materials, if not completely poled, the resultant piezoelectric properties, especially piezoelectric charge coefficient (d_{33}), will be very low. Also, it is clear that the poling process is not applicable to non-ferroelectric materials. That is why high-performance piezoelectric materials must be ferroelectric in the first place.

1.4 Piezoelectric Parameters

1.4.1 Piezoelectric Constants

1.4.1.1 Piezoelectric Charge (Strain) Constant

The piezoelectric charge coefficient relates the electric charge generated per unit area with an applied mechanical force and is expressed in the unit of Coulomb/Newton (C/N) [7, 22]. This constant is most frequently used to evaluate the goodness of a piezoelectric material.

$$d = \frac{\text{Strain developed}}{\text{Applied field}} = \frac{\text{Charge density (open circuit)}}{\text{Applied stress}} \tag{1.3}$$

The d constant is associated with three important materials properties through the following the equation:

$$d = k\sqrt{\varepsilon_0 k^{\mathrm{T}} s^{\mathrm{E}}} \quad (\mathrm{C/N}) \tag{1.4}$$

where k is electro-mechanical coupling coefficient, k^{T} denotes relative dielectric constant at a constant stress, and s^{E} is elastic compliance (10 m/N) at a constant electrical field.

There are two important d constants:

$$d_{31} = k_{31}\sqrt{\varepsilon_0 k_3^{\mathrm{T}} s_{11}^{\mathrm{E}}} \quad (\mathrm{C/N}) \tag{1.5}$$

$$d_{33} = k_{33}\sqrt{\varepsilon_0 k_3^{\mathrm{T}} s_{33}^{\mathrm{E}}} \quad (\mathrm{C/N}) \tag{1.6}$$

It is useful to remember that large d constants relate to large mechanical displacements, which are usually sought in motional transducer devices. Conversely, the coefficient may be viewed as relating the charge collected on the electrodes, to the applied mechanical stress. d_{33} applies when the force is along the three direction (parallel with the polarization axis) and is impressed on the same surface from which the charge is collected. d_{31} applies when the charge is collected from the same surface as with d_{33}, but the force is applied at right angles to the polarization axis. It is commonly known that they have the following empirical relation.

$$d_{33} \approx -2.5 \cdot d_{31} \tag{1.7}$$

1.4.1.2 Piezoelectric Voltage Coefficient (G-constant)

The piezoelectric voltage coefficient is also called voltage output constant, which is defined as the ratio of the electric field produced to the mechanical stress applied and is expressed in the unit of voltage-meter/Newton (Vm/N).

$$g = \frac{\text{Strain developed}}{\text{Applied charge density}} = \frac{\text{Field developed}}{\text{Applied mechanical stress}} \tag{1.8}$$

The g-constants are calculated from the piezoelectric charge (strain) constant (d) and relative permittivity (ε) from the equation:

$$g = \frac{d}{\varepsilon} \ \text{(Vm/N)} \tag{1.9}$$

Depending on the type of relative directions, the g constant can be categorized as g_{33}, g_{31}, or g_{15}, corresponding to d_{33}, d_{31}, or d_{15}, respectively.

1.4.2 Piezoelectric Coupling Coefficient

The piezoelectric coupling coefficient (sometimes referred as the electromechanical coupling coefficient) is defined as the ratio of the mechanical energy accumulated in response to an electrical input or vice versa. It also corresponds to the fraction of electrical energy that can be converted into mechanical energy and vice versa. Thus, the piezoelectric coupling coefficient can be expressed by the following equation:

$$x = \sqrt{\frac{\text{Mechanical energy stored}}{\text{Electrical energy applied}}} = \sqrt{\frac{\text{Electrical energy stored}}{\text{Mechanical energy applied}}} \tag{1.10}$$

The coupling factor can be calculated based on the measured resonance and anti-resonance frequencies of a piezoelectric element, depending on the vibration mode at which the element is excited. The most used coupling factors are k_p and k_t for the vibration along the radial and thickness directions in a circle-shaped disk, respectively. In general, a useful parameter k_eff is frequently used to express the effective coupling coefficient of an resonator with an arbitrary shape, either at its fundamental resonance or at any overtone modes, and is expressed as follows:

$$k_\mathrm{eff}^2 = 1 - \left(\frac{f_\mathrm{r}}{f_\mathrm{a}}\right)^2 \tag{1.11}$$

where f_r and f_a stand for resonating frequency and anti-resonating frequency, respectively. The coupling coefficients can be calculated for the various modes of vibration from the following equations:

$$\frac{k_\mathrm{p}^2}{1-k_\mathrm{p}^2} = \frac{(1-\sigma^\mathrm{E})J_1\left[\eta_1\left(1+\frac{\Delta F}{F_\mathrm{r}}\right)\right] - \eta_1\left(1+\frac{\Delta F}{F_\mathrm{r}}\right)J_0\left[\eta_1\left(1+\frac{\Delta F}{F_\mathrm{r}}\right)\right]}{(1+\sigma^\mathrm{E})J_1\left[\eta_1\left(1+\frac{\Delta F}{F_\mathrm{r}}\right)\right]} \tag{1.12}$$

where

J	Bessel function of the first kind and zero order
J_1	Bessel function of the first kind and first order
σ^{E}	Poisson's ratio
η_1	Lowest positive root of $(1+\sigma^{\mathrm{E}})\cdot J_1\eta = \eta J_0(\eta)$
F_{r}	Resonance frequency (Hz)
F_{a}	Anti-resonance frequency (Hz)
ΔF	$=F_{\mathrm{a}}-F_{\mathrm{r}}$ (Hz)

Assuming that $\sigma^{\mathrm{E}} = 0.31$ for PZT ceramics and $\eta_1 = 2.05$, the following simplified equations holds:

$$k_{33}^2 = \frac{\frac{\pi}{2}}{1+\frac{\Delta F}{F_{\mathrm{r}}}} \tan \frac{\frac{\pi}{2}\frac{\Delta F}{F_{\mathrm{r}}}}{1+\frac{\Delta F}{F_{\mathrm{r}}}} \tag{1.13}$$

$$\frac{k_{31}^2}{1-k_{31}^2} = \frac{\pi}{2}\left(1+\frac{\Delta F}{F_{\mathrm{r}}}\right) \tan \frac{\pi}{2}\frac{\Delta F}{F_{\mathrm{r}}} \tag{1.14}$$

1.4.3 Mechanical Quality Factor

The mechanical Q_{m} (also referred to as Q) is the ratio of the reactance to the resistance in the series equivalent circuit representing the piezoelectric resonator, which is related to the sharpness of the resonance frequency. The mechanical Q_{m} can be calculated using the equation:

$$Q_{\mathrm{m}} = \frac{f_{\mathrm{r}}}{f_2 - f_1} \tag{1.15}$$

where f_{r} is the resonance frequency, f_1 and f_2 are frequencies at −3 dB of the maximum admittance. The mechanical Q_{m} is also related to the electromechanical coupling factor k, following the equation:

$$Q_{\mathrm{m}} = \frac{1}{2\pi F_{\mathrm{r}} Z_{\mathrm{m}} C_0}\left(\frac{F_{\mathrm{a}}^2}{F_{\mathrm{a}}^2 F_{\mathrm{r}}^2}\right) \tag{1.16}$$

where

F_{r}	Resonance frequency (Hz)
F_{a}	Anti-resonance frequency (Hz)
Z_{m}	Impedance at F_{r} (ohm)
C_0	Static capacitance (Farad)

1.5 Issues for Measuring Piezoelectric Properties

1.5.1 Measurement of Direct Piezoelectric Coefficient Using the Berlincourt Method

One of the most crucial figures of merits characterizing a piezoelectric material is the piezoelectric charge constant, also called the direct piezoelectric coefficient. It reflects the internal generation of electrical charges resulting from an applied mechanical force, as previously mentioned. Basically, the higher the piezoelectric charge constant, the more active a piezoelectric material is. A fast and accurate evaluation of the direct piezoelectric coefficient can be realized by the Berlincourt method associated with a quasi-static piezo d_{33}-meter [6, 28–31]. In this method, sample size or geometric shape becomes a factor that need not be strictly taken into account. Besides, the availability and convenient operation of a d_{33}-meter are obvious, which make it a predominantly used method in practice. However, the name of "Berlincourt method" is often mistaken by some people nowadays as being synonymous with the quasi-static measurements of the direct piezoelectric coefficient. The latter more broadly refers to the methods operating at low or quasi-static frequencies, and its basic principle of was proposed in "Piezoelectric Ceramics" by Jaffe et al. The name of "Berlincourt" actually derives from the researcher, Don Berlincourt, who devoted a lot of effort to the development of the initial commercial d_{33} apparatus based on the quasi-static measurement principle [28].

Here, we consider a simple case of measuring the d_{33} value of a ceramic sample poled along the three-direction (z) to elucidate the mathematical basis for the Berlincourt method. In the common case, the interaction between the mechanical and electrical behavior can be described by the equation $d_{33} = [\delta D_3/\delta T_3]_E$, where D_3 denotes electric displacement along the three-direction (z) and T_3 denotes applied stress also along the three-direction (z). For the practical measurement of d_{33}, this equation can be altered as $d_{33} = [(Q/A)\cdot\cdot\cdot(F/A)] = (Q/F)$, where F is applied force, A is the acting area, and Q is charge developed. It is obvious that d_{33} can be determined via measuring the charge induced by a certain force applied on the piezoelectric samples, while the measurement of the areas can be neglected as they cancel out. It should be noted that a constant electric field as fulfilled in the short-circuit condition is the prerequisite of this measurement. To achieve this condition, a large capacitor across the Device Under Test (DUT) or a virtual-ground amplifier is often embedded in the test system.

Based on the aforementioned consideration, one can easily realize that the d_{33} meter must include at least two parts: the force loading system for applying a small oscillating force, and the electronics for the circuit control and the charge measurement. As shown in Figure 1.5, the force loading system can further be divided to three parts, namely, contact probes, loading actuator, and reference sample [31]. The loading actuator is usually in the form of a loudspeaker type coil, which is cheap and easily controllable using electronic signals. The reference sample is used to monitor the applied force. It should be a piezoelectric material with a known piezoelectric coefficient and under the same force condition as the DUT. Thus, it is always put in

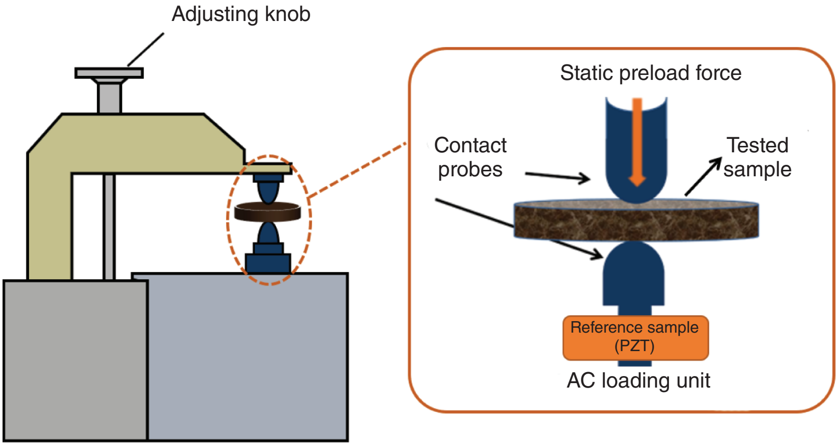

Figure 1.5 Schematic illustration of the components in the force loading system. Source: Modified from Cain [31].

the same loading line. PZT ceramics are usually served as the reference sample due to their high sensitivity. When the DUT is stimulated under the oscillating force with a certain frequency controlled by an amplified AC signal generated by the electronics, the corresponding charge is simultaneously measured by the electronics and the charge detected from the reference sample is converted to the actual force amplitude. Root Mean Squared (RMS) values of these signals are collected to determine the d_{33} value. It is worth nothing that some means of calibration must be conducted to give the correct value as the processing results from RMS signals are only proportional to the d_{33}. Thus, reference calibration sample with a certified value is usually used. Finally, the electronics display a digital readout of the calculated d_{33} value.

The main advantage of the Berlincourt method lies in its simplicity. However, due to its simplicity, anyone can design their own measurement systems and no uniform standard about this method were established. We have found various commercial systems with different measurement performance. Though it is still reliable to compare the results measured in the same apparatus, large variabilities exist in the test results from different measurement systems. There are several factors controlling the accuracy and reliability of the results associated with the Berlincourt method. This issue might be briefly introduced by taking, for example, the magnitude and frequency of the applied AC load force. The magnitude of the force does not make much difference as long as if the piezoelectric sample behaves linearly within the stress range. Nonetheless, the increased magnitude of the force is expected to generate a larger charge signal, which helps increase the signal to noise ratio. It is thus better to set the force to at high levels as long as it can still keep the piezoelectric operating in the linear regime. For a typical Berlincourt type instrument, the frequency of the stimulus force usually ranges from 10 Hz to 1 kHz. This range is governed by both the charge measurement system (for the lower limit) and the force loading system (for the upper limit). The frequency for the mechanical or electrical resonance should be avoided in case of the corresponding measurement anomalies. Thus, some specific frequencies are not used in some countries, such as 97 Hz in the United Kingdom and 110 Hz in the United States. The frequency response also varies in different materials, which can result in a frequency dependent gain issue. At the low frequency range, the measured d_{33} for "soft" piezoelectric materials usually show a pronounced downturn behavior with increasing frequency. This can be attributed to the inhibited domain movement induced by the increasing frequencies, which is depicted by the Rayleigh law. In contrast, the measured d_{33} for "hard" piezoelectric materials often appears to increase linearly with the frequency as the domain wall motion is not dominant in the low frequency range. This latter behavior is tentatively assumed to be influenced by the proximity to resonance peaks in the kHz region.

In summary, the quasi-static method is very simple and straightforward. If the relative magnitudes of the charge output and the applied small oscillating force can be measured, one can easily read d_{33} value by reference to a sample with a known and certificated piezoelectric coefficient.

1.5.2 Measurement of Converse Piezoelectric Coefficient by Laser Interferometer

The displacement of piezoelectric materials under an electric field is concerned as piezoelectric materials usually serve as actuators. However, the displacement is too small to be easily measured in a routine method. With very high resolution and no need for calibration on the length scale, optical interferometry provides the chance for the precise measurement of small displacements within units of nanometer [31–35]. Besides, optical interferometry can achieve the measurement without mechanical contact. Interferometry techniques for the detection of strains have been developed for nearly 50 years. However, at present, this method is still mainly used in research laboratories due to its high price and the need of vibration insulation system.

Piezoelectric coefficients can be measured using single beam, double beam, and heterodyne laser interferometers. For simplicity, the principle for the case based on a single beam laser interferometer is mainly discussed here.

Figure 1.6 depicts the schematic diagram of a Michelson interferometer. When a monochromatic light of wavelength λ interferes with a reference beam, the interference light intensity can be described as follows:

$$\begin{aligned} I &= |E_\mathrm{p}(t) + E_\mathrm{r}(t)|^2 = |E_{\mathrm{p}0} e^{i\{wt-2k(d+\Delta d)\}} + E_{\mathrm{r}0} e^{i(wt-2kd)}|^2 \\ &= E_{\mathrm{p}0}^2 + E_{\mathrm{r}0}^2 + 2E_{\mathrm{p}0}E_{\mathrm{r}0}\cos(2k\Delta d) = I_\mathrm{p} + I_\mathrm{r} + 2\sqrt{I_\mathrm{p} I_\mathrm{r}}\cos(4\pi\Delta d/\lambda) \end{aligned} \tag{1.17}$$

where I_p and I_r are the intensities of the probing and reference beams, respectively, Δd is the optical path-length difference between the two beams, and $k = 2\pi/\lambda$ is the wave number. Actually, the abovementioned relation can be converted into the formula with the parameters, the maximum and minimum interference light intensities I_max and I_min, which can be measured by a photo-detector.

$$I = 1/2\,(I_\mathrm{max} + I_\mathrm{min}) + 1/2\,(I_\mathrm{max} - I_\mathrm{min})\,\cos(4\pi\Delta d/\lambda) \tag{1.18}$$

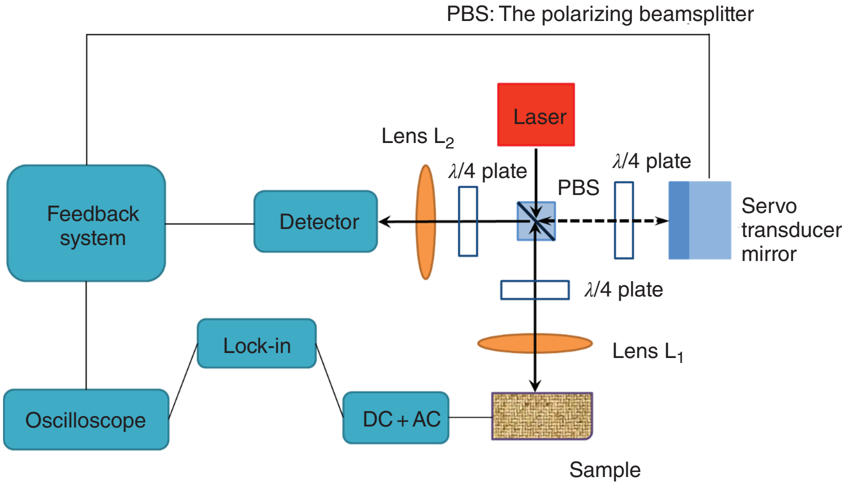

Figure 1.6 Schematic diagram of Michelson interferometer for the measurement of displacement.

In a photodetector, the corresponding photodiode output is determined by the light intensity related to the optical path-length Δd, which is directly related with the sample displacement. An amplified output voltage signal corresponding to the displacement can be obtained, which is usually monitored by an oscilloscope. A definite relationship exists between the voltage output and the displacement. According to the relationship, interferometer sensitivity can be actually set to a specific value, say, 10 nm/V. The changes of the sample dimension are induced by the connection and the disconnection of voltage to the sample. The dimension changes by the identical applied voltage are measured multiple times. The averaged measured value and the connected voltage are used to calculate the piezoelectric charge constant d_{33}, which is governed by the following equation:

$$d_{33} = \Delta l/U \tag{1.19}$$

where U is the applied voltage and Δl is the change of length determined by multiplying the voltage output of the interferometer and its sensitivity.

Single Beam Michelson interferometers are widely used by different research groups to measure piezoelectric and electrostrictive strains. It should be noted that there are various factors, including sample shape and optical alignment, which can affect the measurement validity and accuracy. To obtain the actual value of the sample dimension change parallel to the laser beam, it should be ensured that only the front surface of a sample can move while the back surface of the sample is fixed, and the sample dimension along the lateral direction can expand and contract freely. Due to these requirements, the specimen shape and dimensions are limited. The bulk sample is usually in the form of a cylinder or a thin plate with a suitable ratio between the lateral dimension and the thickness. If this ratio is very large, the clamping effect and the sample bending effect will become significant. One should not neglect such an impact because the resultant errors can even surpass the longitudinal piezoelectric displacement. When measuring the d_{33} of a thin film deposited on a very thick substrate, the clamping effect should be concerned as the substrate bonding is usually assumed to be infinitely rigid. The measured d_{33} is actually the effective converse longitudinal piezoelectric coefficient $d_{33,\text{eff}}$, which can be determined as follows:

$$d_{33,\text{eff}} = d_{33} - 2d_{31}\frac{s_{13}^{\text{E}}}{s_{11}^{\text{E}} + s_{12}^{\text{E}}} \tag{1.20}$$

where S_{ij} is the mechanical compliance of the piezoelectric film and d_{31} is the transverse piezoelectric coefficient.

Proper mounting of the sample is also very important to obtain the actual piezoelectric coefficients. It has been reported that the measured d_{33} of the same disk specimen of PC5H (Morgan Electro Ceramics) showed different values ranging from 750 to 1250 pC/N when simply changing the way the sample was mounted [34]. The accuracy is also strongly affected by small vibrations or abnormal conditions during the measurement. Thus, the measurements using the laser interferometry should be carried out with great caution and patience, though this type of measurement method is simply based on acquiring the displacement value of the sample surface induced by the corresponding applied voltage.

1.5.3 Resonance and Anti-resonance Method

Both the quasi-static method and the laser interferometry method are used for the direct measurements of d_{33}/d_{31}. In contrast to the two aforementioned methods, the resonance and anti-resonance method, or the frequency method can be applied to determine the complete tensor matrix of the material coefficients [21, 36, 37]. These coefficients can be derived by the raw set of measured parameters including resonant frequencies, density, and sample dimensions. The detailed procedure for the determination of these coefficients can be found in the European standard EN 50324-2:2002 and the world standard CEI/IEC 60483:1976.

For this method, an accurate impedance analyzer is a crucial requirement as use for the testing of the resonant frequencies f_{s} and antiresonant frequencies f_{a} as well as the free capacitance C^{T} at 1 kHz. The commercially available lineups of impedance analyzers differ in terms of frequency range and sensitivity. The most regularly used one are, for example, Agilent E4294A and Wayne Kerr 65120B, produced by Agilent and Wayne Kerr, respectively. The other thing to notice is that a set of samples in the forms of a disk, a plate, and a cylinder, which have different vibration modes, should be prepared before the measurements are carried out. Obtaining all the needed sample items from a single bulk material of appropriate size is preferred. The sample dimensions should conform to the world standard CEI/IEC 60483:1976.

Material constants such as piezoelectric coefficient d, dielectric coefficient ε, and elastic coefficient s are anisotropic in general. They are usually described by tensor components written in a simplified matrix form according to the point-group symmetry of the materials. For piezoelectric ceramics, the complete matrix of the coefficients of electromechanical properties can be written as follows:

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ D_1 \\ D_2 \\ D_3 \end{bmatrix} = \begin{bmatrix} s_{11}^{\mathrm{E}} & s_{12}^{\mathrm{E}} & s_{13}^{\mathrm{E}} & & & & & & d_{31} \\ s_{12}^{\mathrm{E}} & s_{11}^{\mathrm{E}} & s_{13}^{\mathrm{E}} & & & & & & d_{31} \\ s_{13}^{\mathrm{E}} & s_{13}^{\mathrm{E}} & s_{33}^{\mathrm{E}} & & & & & & d_{33} \\ & & & s_{55}^{\mathrm{E}} & & & & d_{15} & \\ & & & & s_{55}^{\mathrm{E}} & & d_{15} & & \\ & & & & & 2\cdot(s_{11}^{\mathrm{E}} - s_{12}^{\mathrm{E}}) & & & \\ & & & & d_{15} & & & & \\ & & & d_{15} & & & & & \\ d_{31} & d_{31} & d_{33} & & & & & & \end{bmatrix} \cdot \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \\ E_1 \\ E_2 \\ E_3 \end{bmatrix} \tag{1.21}$$

Based on the IEEE standards [22], the requirement of the sample dimensions and the complete matrix of piezoelectric constants can be established as illustrated in Figure 1.7 [37].

After acquiring the entry parameters, namely, resonant frequencies, antiresonant frequencies, capacitance, density, and sample dimensions, we can calculate the electromechanical coupling coefficients, according to which elastic coefficients s_{11}^{E},

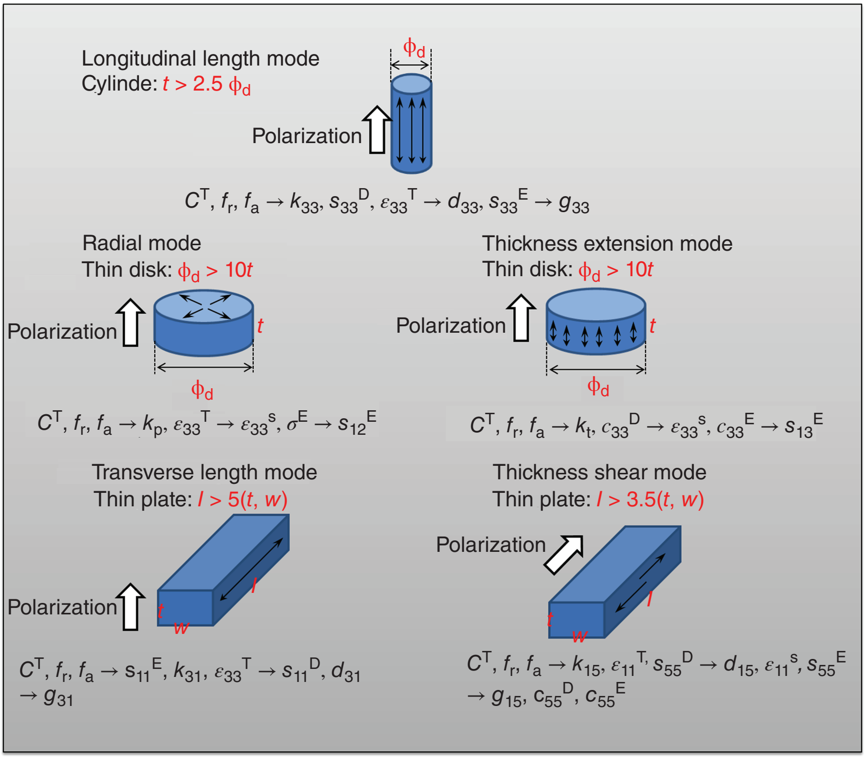

Figure 1.7 Establishing the complete set of material coefficients defined by IEEE standards [37]. Source: Reprinted with permission from Fialka and Benes [37]. Copyright 2013, IEEE.

s_{12}^{E}, s_{13}^{E}, s_{33}^{E}, s_{55}^{E}, and s_{66}^{E} can be derived. As an example, the related formulas for the calculation of the elastic coefficient s_{33}^{E}, the piezoelectric charge coefficient d_{33}, and the piezoelectric voltage coefficient g_{33} for the longitudinal length mode in the cylinder are deduced based on the IEEE standards as follows:

$$s_{33}^{\mathrm{E}} = \frac{s_{33}^{\mathrm{D}}}{1 - k_{33}^2} = \frac{\frac{1}{4 \cdot \rho \cdot f_{\mathrm{p}}^2 \cdot t^2}}{1 - \frac{\pi}{2} \cdot \frac{f_{\mathrm{r}}}{f_{\mathrm{a}}} \cdot \tan\left(\frac{\pi}{2} \cdot \frac{f_{\mathrm{a}} - f_{\mathrm{r}}}{f_{\mathrm{a}}}\right)} \tag{1.22}$$

$$\begin{aligned} d_{33} &= k_{33}(\varepsilon_{33}^{\mathrm{T}} \cdot s_{33}^{\mathrm{E}})^{\frac{1}{2}} = \left(\varepsilon_{33}^{\mathrm{T}} \cdot s_{33}^{\mathrm{D}} \cdot \frac{k_{33}^2}{1 - k_{33}^2}\right)^{\frac{1}{2}} \\ &= \left(C^{\mathrm{T}} \cdot \frac{t}{\frac{\pi \cdot d^2}{4}} \cdot \frac{1}{4 \cdot \rho \cdot f_{\mathrm{p}}^2 \cdot t^2} \cdot \frac{\frac{\pi}{2} \cdot \frac{f_{\mathrm{r}}}{f_{\mathrm{a}}} \cdot \tan\left(\frac{\pi}{2} \cdot \frac{f_{\mathrm{a}} - f_{\mathrm{r}}}{f_{\mathrm{a}}}\right)}{1 - \frac{\pi}{2} \cdot \frac{f_{\mathrm{r}}}{f_{\mathrm{a}}} \cdot \tan\left(\frac{\pi}{2} \cdot \frac{f_{\mathrm{a}} - f_{\mathrm{r}}}{f_{\mathrm{a}}}\right)}\right)^{\frac{1}{2}} \end{aligned} \tag{1.23}$$

$$g_{33} = \frac{d_{33}}{\varepsilon_{33}^{\mathrm{T}}} = \frac{d_{33}}{C^{\mathrm{T}} \cdot \frac{t}{\frac{\pi \cdot d^2}{4}}} \tag{1.24}$$

where f_{r} is the resonance frequency, f_{a} is anti-resonance frequency, and f_{p} is parallel resonant frequency.

The frequency method is advantageous since it can determine the complete matrix of the material coefficients, though a complete set of samples needs to be manufactured. The accuracy of the calculated coefficients depends on the overall measurement accuracy of the initial parameters including resonant frequencies, anti-resonant frequencies, density, and sample dimensions. Besides, it is worth nothing that the measured samples should comply with a minimum aspect ratio stipulated by the IEEE standards.

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