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Piezoelectric Materials and Their Applications

Part 1. Definitions and Measurements
Piezoelectric Materials and Their Applications

D.F. Jones¹, S.E. Prasad² and J.B. Wallace³

¹ Defence Research Establishment Atlantic
Dartmouth, Nova Scotia, Canada
B2Y 3Z7

² Sensor Technology Limited
P.O. Box 97
20 Stewart Road
Collingwood, Ontario, Canada
L9Y 3Z4

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Abstract: Over 100 years ago, Jacques and Pierre Curie experimentally confirmed the presence of the piezoelectric effect in quartz, Rochelle salts and tourmaline single crystals. Within the last 50 years, a number of ceramic and polymer materials with non-symmetrical crystal structures have also been found to exhibit the piezoelectric effect. The discovery of strong piezoelectricity in these materials has led to their commercialization and has been a major factor in the development of a wide range of applications. This paper begins with a review of the fundamental properties of piezoelectric materials. A description of the important types of piezoelectric materials and their characteristics are presented next, followed by discussions of selected applications, with additional applications listed in tabular format.
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<tr>
<td>I</td>
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</tr>
<tr>
<td>L</td>
<td>Inductance</td>
<td>henry $\text{H}$</td>
</tr>
<tr>
<td>M</td>
<td>Mass</td>
<td>gram $g$</td>
</tr>
<tr>
<td>N</td>
<td>Force</td>
<td>newton $\text{N}$</td>
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<tr>
<td>$N_1$, $N_2$, $N_3$</td>
<td>Frequency constants</td>
<td>hertz$\cdot$meter $\text{Hz$\cdot$m}$</td>
</tr>
<tr>
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<td>At constant electric polarization</td>
<td>coloumb/(meter)$^2$ C/m$^2$</td>
</tr>
<tr>
<td>$P_p$, $P_2$</td>
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<td></td>
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<tr>
<td>$Q_M$</td>
<td>Mechanical quality factor</td>
<td>ohm $\Omega$</td>
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<tr>
<td>$R_1$, $R_2$, $R_\beta$, $R_\alpha$</td>
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<td>(meter)$^2$/newton $\text{m}^2$/N</td>
</tr>
<tr>
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<td>Elastic compliance constants</td>
<td></td>
</tr>
<tr>
<td>$t$ (superscript)</td>
<td>At constant strain</td>
<td></td>
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<td></td>
</tr>
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<td>$t_1$, $t_2$</td>
<td>Time</td>
<td>day</td>
</tr>
<tr>
<td>$\tan \delta$</td>
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<td></td>
</tr>
<tr>
<td>$T_1$, $T_2$, $T_3$</td>
<td>Stress components</td>
<td></td>
</tr>
<tr>
<td>$T_0$</td>
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<td></td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
<td></td>
</tr>
<tr>
<td>$v_1$, $v_2$</td>
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<td></td>
</tr>
<tr>
<td>w</td>
<td>Width</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>Admittance</td>
<td></td>
</tr>
<tr>
<td>$Y_{11}$, $Y_{33}$</td>
<td>Elastic modulus</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>Impedance</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Permittivity of free space</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>Root of a Bessel equation</td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Poisson’s ratio</td>
<td></td>
</tr>
</tbody>
</table>
2. INTRODUCTION

Piezoelectricity may be described as the property possessed by some materials that become electrically charged when subjected to a mechanical stress. These materials also show the converse effect by undergoing mechanical deformation due to the application of an electric field. The origin of the piezoelectric effect is related to an asymmetry in the unit cell and the resultant generation of electric dipoles due to mechanical distortion.

The discovery of piezoelectricity in ceramics allowed for the manufacture of relatively inexpensive piezoelectric elements for utilization in commercial transducer applications. Since a wide range of electromechanical properties can be obtained by altering the formulation of these ceramics, a number of unique piezoelectric compositions are commercially available for different applications. Such materials include lead zirconate titanate, lead metaniobate, lead titanate and modifications of these compositions. These lead-based ceramics are usually prepared using standard ceramic processing techniques.

Lead zirconate titanate, for example, is produced by thoroughly mixing proportional amounts of high quality lead, zirconium and titanium based oxide and/or carbonate powders using specialized milling techniques. The mixing process ensures a homogeneous reaction of the precursor powders when heated to temperatures ranging between 800-1000 °C. During this heat treatment, the oxides and/or carbonate powders react to form the perovskite lead zirconate titanate powder. Unfortunately, multi-particle bodies (agglomerates) of the reacted powder also form during this reaction. High energy milling is often utilized to break up these agglomerates and reduce the particle size of the reacted powder. By reducing the particle size and increasing the surface area of the powder, its sinterability is increased and a better ceramic can be produced [1].

The resulting reacted and milled powders are usually mixed with a binder and formed into a shape which is as close to the desired shape as possible. During this stage, it is important to consider the degree of shrinkage that will occur during the sintering heat treatment. The amount of shrinkage that occurs during sintering of a given piezoelectric ceramic depends on the composition of the powder being pressed and the shape of the pressed piece. Prior to sintering, the binder must be burned (bisqued) by heating the formed ceramics to temperatures between 500 and 700 °C over an 8 to 12 hour period. After bisquing, the pressed part is ready to be sintered in a final heat treatment. During this stage, the powder particles in the pressed piece can grow and fuse to create a high-density, high-strength ceramic. Although these sintered ceramics are designed to be as close to the final shape as possible, some machining of the ceramic is usually necessary to achieve the desired electromechanical properties. Once the ceramic has been machined to the appropriate dimensions, it can be electroded. Nickel or silver based electrodes are the most common commercially available electrodes. Once the electrodes are in place, the ceramic is poled by applying an external electric field using a thermally assisted process. The poling procedure aligns electric dipoles and creates a remnant polarization in the ceramic.

Once poled, the electromechanical properties of a piezoelectric ceramic can be determined. The density ($\rho$), compliance ($s_{ij}^B$), Curie temperature ($T_c$), dielectric constant ($K^T$), and dielectric loss factor or loss tangent ($\tan \delta$) are all important properties of a piezoelectric ceramic and should be taken into consideration for specific applications. In addition to these measurements, the engineer should also consider how the properties of the ceramic will change with time (ageing rate). The rate of ageing for piezoelectric ceramics depends on the particular composition and usually occurs as a logarithmic function of time.
2.1 Definitions and Terminology

In piezoelectric transducers, the material characteristics depend on the direction of the applied electric field, displacement, stress and strain. Hence superscripts and subscripts to indicate special restraints and directional properties are used with the symbols. The direction of polarization is generally designated as the z-axis of an orthogonal crystallographic system. The axes x, y and z are respectively represented as 1, 2 and 3 directions and the shear about these axes are represented as 4, 5 and 6. This is shown schematically in Fig. 1. The various piezoelectric material constants are generally expressed with subscripts using this notation. Some examples are also shown in Fig. 1. The first subscript gives the direction of the electrical field associated with the voltage applied or the charge produced. The second subscript gives the direction of mechanical stress or strain. Superscripts indicate a constant mechanical or electrical boundary condition. Table 1 gives a general description of the superscripts. In addition to the above, planar, radial and thickness modes are sometimes expressed with a subscripts p, r and t, respectively.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical Stress</td>
<td>T</td>
<td>Mechanically Free</td>
</tr>
<tr>
<td>Electric Field</td>
<td>E</td>
<td>Electrical Short Circuit</td>
</tr>
<tr>
<td>Electric Displacement</td>
<td>D</td>
<td>Electrical Open Circuit</td>
</tr>
<tr>
<td>Mechanical Strain</td>
<td>S</td>
<td>Mechanically Clamped</td>
</tr>
</tbody>
</table>

2.1.1 Density

Density, $\rho$, of a material is expressed as the ratio of the mass to its volume:

$$\rho = \frac{\text{Mass}}{\text{Volume}}.$$  \hspace{1cm} (1)

2.1.2 Curie Temperature

The crystal structure of a material changes at the Curie point from a piezoelectric (non-symmetrical) to a non-piezoelectric (symmetrical) form. This phase change is accompanied by a peak in the dielectric constant-temperature curve at the Curie temperature ($T_C$) which is expressed in degrees Celsius. The Curie temperature limits the range in temperatures that the piezoelectric material can effectively operate.

2.1.3 Dielectric Constant (Relative Permittivity)

The dielectric constant is defined as the ratio of the permittivity of the material to the permittivity of free space. This is generally measured well below the mechanical resonance. The dielectric constant is derived from the static capacitance measurements at 1 kHz using a standard impedance bridge. The relations are expressed (Fig. 2) as:
Figure 1: Piezoelectric Symbols and Terminology
Figure 2: Notation for Relative Permittivity
\[
\frac{K^T}{\varepsilon_0} = \frac{C_0 h}{\varepsilon_r A}
\]  

where \(K^T\) is the relative dielectric constant of the piezoelectric material, \(\varepsilon_0\) is the relative permittivity of free space (8.854 \times 10^{-12} \text{ F/m}), \(h\) is the distance between electrodes (m), \(A\) is the area of the electrodes (m²) and \(C_0\) is the measured capacitance at 1 kHz (F).

### 2.1.4 Dielectric Loss Factor (Loss Tangent)

The dielectric loss factor is defined as the tangent of the loss angle (\(\tan \delta\)). The loss factor represents the ratio of resistance to reactance of a parallel equivalent circuit of the ceramic element (Fig. 3a). The loss factor can be measured directly using an impedance bridge. The dielectric loss factor is a measure of the amount of electrical energy which is lost through conduction when a voltage is applied across the piezoelectric element. Most applications require piezoelectric materials with low dielectric loss factors.

### 2.1.5 Mechanical Quality Factor

The most common method of determining the resonance properties of a piezoelectric material involves measuring the impedance (or admittance) of the material as a function of frequency. The impedance of the piezoelectric material passes through a minimum at the resonance frequency and a maximum at the antiresonance frequency. Between the resonance (\(F_r\)) and antiresonance (\(F_a\)) frequencies the piezoelectric material behaves inductively; while below \(F_r\) and above \(F_a\) the piezoelectric material behaves as a capacitor. The mechanical quality factor (\(Q_m\)) is defined as the ratio of the reactance to the resistance in the series equivalent circuit representing the piezoelectric resonator (Fig. 3b). The \(Q_m\) can be used to determine the sharpness of the resonance peak, i.e. the larger the \(Q_m\), the sharper the resonance peak. The \(Q_m\) is also related to the sharpness of the resonance frequency:

\[
Q_m = \frac{F_r^2}{2\pi F_r Z_m C_0 \left( \frac{F_a}{F_r^2} \right)}
\]  

where \(F_r\) is the resonance frequency in hertz (Hz), \(F_a\) is the antiresonance frequency in hertz, \(Z_m\) is the impedance in ohms (Ω) at \(F_r\) and \(C_0\) is the static capacitance in Farads (F).

Alternatively, \(Q_m\) can also be determined using the equation:

\[
Q_m = \left( \frac{F_r}{F_1 - F_2} \right)
\]

where \(F_1, F_2\) are the frequency values at the points where the electrical conductance falls to half its value at the resonance frequency, \(F_r\).

### 2.1.6 Frequency Constants

The frequency constant, \(N\), is the product of the resonance frequency and the linear...
Figure 3: Equivalent Circuit of a Piezoelectric element (Non-Resonance Operation)

a). Parallel

b). Series
dimension governing the resonance. The various modes of resonance, illustrated in Fig. 4, are:

\[ N_1 = F_r D \quad \text{(Hz.m) Radial Mode Disc} \quad (5) \]

\[ N_2 = F_r L \quad \text{(Hz.m) Length Mode Plate} \quad (6) \]

\[ N_3 = F_r L \quad \text{(Hz.m) Length Mode Cylinder} \quad (7) \]

\[ N_4 = F_r h \quad \text{(Hz.m) Thickness Mode Disc, Plate} \quad (8) \]

\[ N_5 = F_r h \quad \text{(Hz.m) Shear Mode Plate} \quad (9) \]

2.1.7 Piezoelectric Coupling Coefficients

The coupling coefficient (sometimes referred to as the electromechanical coupling coefficient) is defined as the ratio of the mechanical energy accumulated in response to an electrical input or vice versa. The piezoelectric coupling coefficient can be expressed as follows:

\[ k = \sqrt{\frac{\text{Mechanical energy stored}}{\text{Electrical energy applied}}} \quad (10) \]

\[ k = \sqrt{\frac{\text{Electrical energy stored}}{\text{Mechanical energy applied}}} \quad (11) \]

The coupling coefficients can be calculated for the various modes of vibration from the following equation:

\[ k_p^2 = \frac{(1 - \sigma^2)j_0[\eta_1(1 + \frac{\Delta F}{F_r})] - \eta_1(1 + \frac{\Delta F}{F_r})j_0[\eta_1(1 + \frac{\Delta F}{F_r})]}{1 - k_p^2 - (1 + \sigma^2)j_1[\eta_1(1 + \Delta \frac{F}{F_r})]} \quad (12) \]

where \( J_0 \) is the Bessel function of the first kind and zero order, \( J_1 \) is the Bessel function of first kind and first order, \( \sigma \) is Poisson's Ratio and \( \eta \) is the lowest positive root of \((1 + \sigma^2)j_1(\eta) = \eta j_0(\eta)\). If the Poisson’s ratio for lead zirconate titanate is taken to be 0.31 and the lowest possible root is taken to be 2.05, the following approximations can be made for the coupling coefficient:

\[ \frac{k_{31}^2}{1 - k_{31}^2} = \frac{\pi}{2} (1 + \frac{\Delta F}{F_r}) \tan(\frac{\pi}{2} \frac{\Delta F}{F_r}) \quad (13) \]

where \( \Delta F = F_a - F_r \) (Hz).
Figure 4: Piezoelectric Modes of Vibration
Another parameter, $k_{\text{eff}}$, is frequently used to express the effective coupling coefficient of an arbitrary resonator, either at the fundamental resonance or at any overtone and is expressed as follows:

$$
\frac{k_{\text{eff}}^2}{1-k_{\text{eff}}^2} = \frac{F_a^2 - F_r^2}{F_r^2}.
$$

(14)

### 2.1.8 Piezoelectric Charge Coefficients (d-Constant)

The piezoelectric charge coefficient is the ratio of the electric charge generated per unit area to an applied force and is expressed in Coulomb/Newton (C/N). Thus,

$$
d = \frac{\text{Strain developed}}{\text{Applied field}}
$$

or

$$
d = \frac{\text{Charge density (short circuit)}}{\text{Applied stress}}.
$$

(15) (16)

The $d$-constants are calculated from the equation:

$$
d = k \sqrt{K^T s^E} \quad \text{(C/N)}. \tag{17}
$$

Specific $d$-constants include:

$$
d_{31} = k_{31} \sqrt{\varepsilon_0 K_3^T s_{11}^E} \quad \text{(C/N)} \tag{18}
$$

$$
d_{33} = k_{33} \sqrt{\varepsilon_0 K_3^T s_{33}^E} \quad \text{(C/N)} \tag{19}
$$

where $k$ is the electromechanical coupling coefficient, $K^T$ is the relative dielectric constant and $s^E$ is the compliance ($10^{-12}$ m²/N).

### 2.1.9 Piezoelectric Voltage Coefficients (g-Constant)

The piezoelectric voltage coefficient is the ratio of the electric field produced to the mechanical stress applied and is expressed as volt.meter/newton (Vm/N). Thus,

$$
g = \frac{\text{Strain developed}}{\text{Applied charge density}}
$$

(20)
\[ g = \frac{\text{Field developed}}{\text{Applied mechanical stress}}. \quad (21) \]

The \( g \)-constants are calculated from the equation:

\[ g = \frac{d}{\varepsilon} \quad (Vm/N). \quad (22) \]

Specific \( g \)-constants include:

\[ g_{31} = \frac{d_{31}}{\varepsilon \varepsilon_0 K_3} \quad (Vm/N) \quad (23) \]

\[ g_{33} = \frac{d_{33}}{\varepsilon \varepsilon_0 K_3} \quad (Vm/N) \quad (24) \]

where \( d \) is the charge density and \( \varepsilon \) is the relative permittivity.

2.1.10 Elastic Constants

Young's modulus describes the mechanical stiffness properties and is expressed as the ratio of stress to strain. In a piezoelectric material, mechanical stress produces an electrical response which opposes the resultant strain. The value of the Young's modulus depends on the direction of stress and strain and the electrical conditions. The inverse of Young's modulus \( Y \) is the elastic compliance \( s \)

\[ s = \frac{1}{Y} \quad (25) \]

\[ s = \frac{\text{Strain}}{\text{Stress}} \quad (26) \]

\[ s = \frac{1}{\rho v^2} \quad (27) \]

where \( \rho \) is the density \((\text{kg/m}^3)\), \( v \) is the sonic velocity \((\text{m/s})\) and \( l \) is the length of the element \((\text{m})\). Thus for the thickness mode,

\[ s_{33} = \frac{1}{\rho v_1^2} \quad (v_1 = 2\pi F_c l) \quad (28) \]

and
\[ s_{33}^E = \frac{s_{33}^D}{(1 - k_{33}^2)} \]  

while for the radial mode,

\[ s_{11}^E = \frac{1}{\rho v_2^2} \left( \nu_2 = 2\pi f \right) \]  

and

\[ s_{11}^D = (1 - k_{31}^2) s_{11}^E \]  

2.1.11 Ageing Rate

The ageing rate of a piezoelectric ceramic is an index of the change of certain material constants with time (age). The most important constants that age with time are the dielectric constant, frequency constants and the resonance frequency. The ageing of ceramics has a logarithmic function with time, as follows:

\[ \text{Ageing Rate} = \frac{1}{(\log t_2 - \log t_1)} (\frac{P_2 - P_1}{P_1}) \]  

where \( t_1, t_2 \) are the number of days after polarization and \( P_1, P_2 \) the measured parameters which could be the capacitance, resonance frequency, etc.

2.2 Measurement of Piezoelectric Properties

A number of standards have been developed for the measurement of properties of piezoelectric elements including both crystals and ceramics [2-6]. While the IEEE and IEC standards cover the characteristics of the materials, the DOD-STD-1376 also covers such issues as ageing in piezoelectric ceramics, workmanship, chips, etc.

To make accurate measurements of various constants, it is necessary to perform experiments on test specimens which are dimensioned to provide appropriate boundary conditions for the specific piezoelectric modes. These are listed in Table 2.
Table 2: Piezoelectric Material Constants for Different Modes of Vibration

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<tr>
<th>Mode</th>
<th>Specimen Size</th>
<th>Material Constants to be Determined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>( h = 1.0 \text{ mm} ) ( D_0 = 16.0 \text{ mm} )</td>
<td>( k_p, k_3, \tan \delta, \rho, Q_M )</td>
</tr>
<tr>
<td>Thickness</td>
<td>( h = 16.0 \text{ mm} ) ( D_0 = 6.35 \text{ mm} )</td>
<td>( k_{33}, k_3, \tan \delta, \rho, Q_M ) ( d_{33}, g_{33}, s_{33}^D, s_{33}^E )</td>
</tr>
<tr>
<td>Shear</td>
<td>( l = 12 \text{ mm} ) ( w = 10 \text{ mm} ) ( h = 0.2 \text{ mm} )</td>
<td>( k_{31}, k_{3}, \tan \delta, \rho, Q_M ) ( d_{31}, g_{31}, s_{11}^D, s_{11}^E )</td>
</tr>
</tbody>
</table>

2.2.1 Density

Density can be measured using a balance and a micrometer. A buoyancy technique (see Ref. 7) provides better accuracy and has the advantage that measurements can be made on any shape. The density \( \rho \) can be calculated as follows using the volume calculated from piezoelectric elements dimensions:

\[
\rho = \frac{\text{Mass}}{\text{Volume}}. \tag{33}
\]

In addition, the density could also be calculated using the buoyancy technique:

\[
\rho = \frac{\text{Weight of element in air}}{\text{Apparent loss of weight in water}} \tag{34}
\]

2.2.2 Dielectric Constant and Dissipation Factor

The dielectric constant (\( K \)) and dissipation factor (\( \tan \delta \)) can be measured using a standard impedance bridge or an impedance analyzer both of which provide a direct reading. Measurements are generally carried out at 1 kHz to measure static parameters, away from mechanical resonance, at low applied electric field.

2.2.3 Equivalent Circuit

A piezoelectric element operating at or near its resonance frequency can be characterized by the equivalent circuit shown in Fig. 5. The series and parallel resonance frequencies, \( F_s \) and \( F_p \) respectively, are given by the following equations:

\[
F_s = \frac{1}{2\pi} \sqrt{\frac{C_0 + C_1}{L_1 C_0 C_1}} \text{ (Hz) (Parallel Resonance)} \tag{35}
\]
Figure 5: Equivalent Circuit of a Piezoelectric Resonator
2.2.4 Resonance Frequencies

The resonance frequencies can be measured using constant voltage and constant current circuits shown in Fig. 6. The variation of impedance and admittance of the piezoelectric ceramic element as a function of frequency are also shown in Fig. 7. The piezoelectric material behaves capacitively below \( F_r \) and above \( F_a \). Between \( F_r \) and \( F_a \), it behaves inductively. The phase angle of the element also undergoes a sign change at the resonance and antiresonance frequencies and therefore can also be used to determine \( F_r \) and \( F_a \). This is illustrated in Fig. 8.

\[
F_r = \frac{1}{2\pi} \sqrt{\frac{1}{L_1 C_1}} \quad (\text{Hz}) \quad (\text{Series Resonance})
\]
Figure 6: Circuits for Measuring the Resonance Frequencies

a) Constant Voltage Circuit

b) Constant Current Circuit
a) Variation of Impedance with Frequency

b) Variation of Admittance with Frequency

Figure 7: Impedance and Admittance Frequency Characteristics
Figure 8: Phase Angle Frequency Characteristics