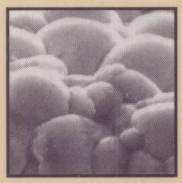

Advances in Dielectric Ceramic Materials

Edited by
K.M. Nair
A.S. Bhalla

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Preface

Conventional ceramic materials are predominantly minerals. However, the development of the electronic industry has led to the formation of a new branch of ceramics, which can be called synthetic ceramics. Extensive investigations of the dielectric and magnetic properties of synthetic inorganic materials, their solid solutions and mixtures produced a variety of materials applicable to electronic devices. Among them, capacitors, transducers, sensors, phase shifters, pyro-detectors, thermistors, memory devices, and medical diagnostic devices are the major areas where new materials developments are needed to compete effectively against polymeric materials. In general, ceramic-based microelectronic devices with specific functions have penetrated all the major industrial electronic markets, such as computers, radar and communication equipment, satellites, aircraft and navigational equipment, military electronics, automotive electronics, and other consumer electronic devices.

With the drive of new initiatives in the areas of advanced applications, and the enhanced demand for materials of better reliability and performances, it is highly desirable to review and project the future direction in materials development, cost-effective preparation techniques and other aspects of advanced materials technology. The American Ceramic Society is a major facilitator for new materials development for electronics through information transfer by bringing together technical experts from diversified fields.

This volume is a collection of selected papers, covering all the pertinent areas of dielectric materials development, presented at the International Symposium on Dielectric Ceramics held during the 99th Annual Meeting of The American Ceramic Society in Cincinnati, OH, May 5–7, 1997. All the papers included in this volume were peer-reviewed.

We, the editors, acknowledge and appreciate the contributions of the symposium organizers, speakers, conference session chairs, manuscript reviewers and Society officials for making this endeavor a successful one.

K.M. Nair
A.S. Bhalla

Contents

HISTORICAL DEVELOPMENT OF PIEZOELECTRIC MATERIALS AND APPLICATIONS

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ABSTRACT

Piezoelectricity was discovered by the brothers Curie in 1880. The piezoelectric effect remained a curiosity until the early 1920s when it was used to realize crystal oscillators. Since then, materials development has made it possible for devices based on this effect to expand dramatically in application. One of the most appealing aspects of piezoelectricity for modern applications is the compelling immediacy and simplicity of the transduction mechanism. A rapidly burgeoning area is the integral incorporation of mechanical actuation and sensing onto electronic chips. These micro-electro-mechanical structures promise signal sensing, processing, and outputting features unattainable by exclusively electronic or photonic means. We present a discussion of this most interesting effect, its history, and particularly the development of piezoelectric materials, with some modern and futuristic applications.

INTRODUCTION

The term "piezoelectricity" refers to the production of bound electrical charges on surfaces of a suitable specimen by the imposition of mechanical stress. One says that the elastic and electric variables are coupled; we shall also find that the effect provides connections between a number of well-known personages, and between some seemingly disparate facts, in a most interesting manner. A good portion of the history is gleaned from Cady's book [1], which can still be read with great profit by those interested in the subject of piezoelectricity. Some of the phenomenology is taken from Ref. [2]. Let us begin with the events outlined in Table I.

Coulomb [3] is said to have conjectured that electricity might be produced by pressure; this led to experiments by Haüy [4] and A C Becquerel [5] with inconclusive results; any charges produced might have been caused by friction or contact electricity. Becquerel did make a prescient remark in respect to charges

occasioned by stretching rubber; he conjectured that experiments with crystalline minerals might show effects due to their anisotropy [8].

TABLE I. Schematic history of piezoelectricity

Coulomb	conjecture
Haüy	experiments
Becquerel	experiments, 1820
Curie, P. & J.	discovery, 1880
Hankel	"piezoelectricity," 1881
Lippmann	converse effect, 1881; found by Curies, 1881; same coefficient
Kelvin	atomic model, 1893;
Duhem	phenomenological
Pockels	theory
Voigt	1894,"tensor;" Lehrbuch, 1910
Langevin	sonar, c. 1914-1918; ultrasonics
Born	theoretical calculation-e of β-ZnS, 1920

The undoubted discoverers of the phenomenon of piezoelectricity were the Curie brothers. They knew what they were looking for, and had the backgrounds and facilities to bring the search to a successful conclusion [9]. Their pictures appear as the frontispiece in Cady, and in Ref. [10]. They announced their discovery as follows:

"Those crystals having one or more axes whose ends are unlike, that is to say hemihedral crystals with oblique faces, have the special physical property of giving rise to two electrical poles of opposite signs at the extremities of these axes when they are subjected to a change in temperature: this is the phenomenon known under the name of *pyroelectricity*."
"We have found a new method for the development of polar electricity in these same crystals, consisting in subjecting them to variations in pressure along their hemihedral axes."

P. & J. Curie

"Development by pressure of polar electricity in hemihedral crystals with inclined faces," Bull. soc. min. de France, vol. 3, pp. 90-93, 1880. Read on April 8, 1880. Quoted in Cady, Piezoelectricity, 1946. See also [10a].

Additional perspective on the state of science at the time of the Curie's discovery is provided by considering that it was only by 1880 that Mendeleev's periodic chart of the elements came to be universally accepted, whereas his inspiration occurred in 1869 [10b].

In 1881, Hankel [11] suggested the name "piezoelectricity," which was accepted by all. Also in 1881, Lippmann [12], on thermodynamic grounds, asserted that the converse effect should exist as well, that is, imposition of surface charge induces mechanical deformation. The Curies verified this in the same year,

and showed that the coefficients for both the direct and converse effects were identical.

Lord Kelvin [13] developed an atomic model to describe the effect in 1893 [14]; this is explained and expanded in Ref. [15]. The phenomenology of piezoelectricity was advanced substantially by Duhem [16] and Pockels [17], but with the work of Woldemar Voigt [18-20] it can be said to have reached maturity.

During the period 1914-1918, Langevin [22] applied piezoelectric transducers to the problem of submarine detection; he thus became the father of sonar and of the discipline of ultrasonics. Born [24], in 1920, published the first lattice-theoretical calculation of a piezoelectric coefficient, that of β-ZnS. See also [24a].

The piezoelectric effect remained largely a curiosity until 1921 when Cady [25] utilized its presence in quartz to realize crystal resonators for the stabilization of oscillators. See also [26]. Bechmann [27], one of the four independent discoverers of the zero-temperature-coefficient AT and BT cuts of quartz in the period 1933-34, contributed greatly to the field of frequency control. Another estimable contributor to many areas of applied piezoelectricity was Mason [28]. In Ref. [15] he explained and extended the Kelvin model; he invented the quartz GT cut in 1940, and is responsible for the equivalent circuit model that bears his name.

POINT GROUPS AND CURIE SAMPLES

Piezoelectricity is found in many substances, such as bone, wood, and ice. Because of its polar nature, it depends on an asymmetry in the structure of the material. Most piezoelectrics are crystals, and it is found that the effect depends upon the crystallographic symmetry, in particular, that of the point groups. Figure 1 shows the thirty-two point groups [31]; the twenty piezoelectric groups are those under the heading 'acentric,' with the exception of class 432. The point group also establishes the forms of the elastic, piezoelectric, and dielectric matrices. Additional details are given in Refs. [32-39]. In Table II are listed the samples reported by the Curies in 1880 along with the point group. Topaz is usually accorded symmetry mmm. One sees the well-placed representation of groups in their sample.

In 1925, G Heckmann of Göttingen published a very instructive schematic representation of couplings between elastic, electric, and thermal variables [40]; these have been modified and embellished by others ever since [41]. A version of the Heckmann diagram is shown in Fig. 2.

CONSTITUTIVE EQUATIONS

The phenomenological equations that govern the linear macroscopic behavior of piezoelectrics are listed in matrix form in Table III; a prime denotes transpose.

CRYSTAL SYSTEM	CENTRIC POINT GROUPS		ACENTRIC POINT GROUPS					OPTIC AXES
			POLAR		NONPOLAR			
TRICLINIC	$\bar{1}$		1		NONE			BIAXIAL
MONOCLINIC	2/m		2	m	NONE			
ORTHORHOMBIC	mmm		mm2		222			
TETRAGONAL	4/m	4/mmm	4	4mm	$\bar{4}$	$\bar{4}$2m	422	UNIAXIAL
TRIGONAL	$\bar{3}$	$\bar{3}$m	3	3m	32			
HEXAGONAL	6/m	6/mmm	6	6mm	$\bar{6}$	$\bar{6}$m2	622	
CUBIC	m3	m3m	NONE		23	$\bar{4}$3m	432	ISOTROPIC
	11 GROUPS		10 GROUPS		11 GROUPS			

Figure 1. The thirty-two crystallographic point groups

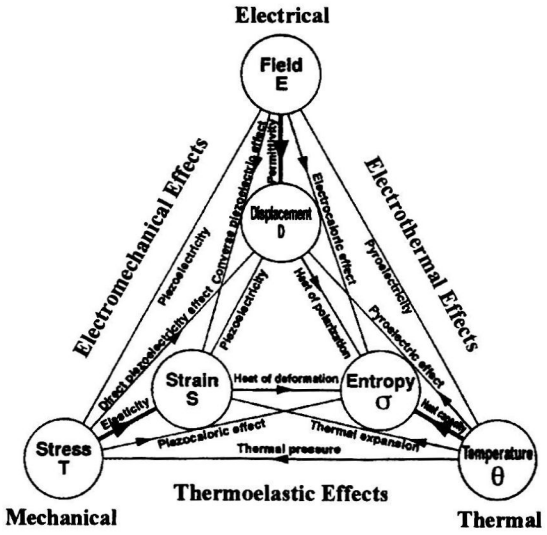

Figure 2. Heckmann diagram relating intensive (outer triangle) and extensive (inner triangle) variables.

The third set ($S = s^E T + d' E$) says that stress (T) is proportional to strain (S); Ref. [44], and also is proportional to electric field; this represents the converse effect; the piezo portion of its companion ($D = d T + \varepsilon^T E$), represents the direct effect. One sees that the piezoelectric coefficient that couples the mechanical and electrical variables is the same in both equations, as the Curies found.

TABLE II. Crystals measured by the Curie brothers for the presence of piezoelectricity

Crystal	Formula	Class
zincblende/sphalerite	β-ZnS	4 3 m
sodium chlorate	$Na\ Cl\ O_3$	2 3
boracite	$Mg_3\ B_7\ O_{13}\ Cl$	4 3 m
tourmaline	$Na\ Mg_3\ B_3\ Al_6\ Si_6\ O_{27} \bullet (OH)_4$	3 m
quartz	$Si\ O_2$	3 2
calamine/hemimorphite	$Zn_4\ (OH)_2\ Si_2\ O_7 \bullet H_2\ O$	mm2
topaz	$Al_2\ Si\ O_4\ (F, OH)_2$	mm2 ?
Rochelle Salt/sodium potassium tartarate	$K\ Na\ (C_4\ H_4\ O_6) \bullet 4\ H_2\ O$	222
tartaric acid	$H_2\ C_4 \bullet H_4\ O_6$	2
cane sugar/sucrose	$C_{12}\ H_{22}\ O_{11}$	2

TABLE III. Elasto-piezo-dielectric constitutive equations

$T = c^E S - e' E$	$D = e S + \varepsilon^S E$
$T = c^D S - h' D$	$E = -h S + \beta^S D$
$S = s^E T + d' E$	$D = d T + \varepsilon^T E$
$S = s^D T + g' D$	$E = -g T + \beta^T D$

The first set written out in tensor notation is:

$$T_\lambda = c^E{}_{\lambda\mu}\ S_\mu - e_{m\lambda}\ E_m$$
$$D_m = e_{m\lambda}\ S_\lambda + \varepsilon^S{}_{mj}\ E_j$$

It was Voigt who first converted the second-rank, three-dimensional stress and strain tensors into first-rank, six-dimensional tensors so that the constitutive equations given above could be represented in two-dimensional form. Matrices are simpler than three-dimensional stacks!

The choice of independent variables determines the particular piezoelectric constant, as is seen in Table III. The names and units of the most often used piezoelectric constants are given in Table IV. The 'a' and 'b' constants are used when polarization is used as a variable in place of electric field, E, or electric displacement, D. The polarization coefficients are used primarily for electro-optical applications.

The different elastic, piezoelectric, and dielectric coefficients are interrelated. For point group 6mm, which includes poled ceramics [45], the difference relations are written out explicitly from the matrices given in, e.g., Refs. [1, 20, 30, 34, 43], as follows:

$$c_{11}^{D} - c_{11}^{E} = e_{31}^{2}/\varepsilon_{33}^{S}\ ;\ c_{12}^{D} - c_{12}^{E} = e_{31}^{2}/\varepsilon_{33}^{S}$$
$$c_{13}^{D} - c_{13}^{E} = e_{33}^{2}/\varepsilon_{33}^{S}\ ;\ c_{44}^{D} - c_{44}^{E} = e_{15}^{2}/\varepsilon_{11}^{S}$$
$$c_{66}^{D} - c_{66}^{E} = 0; \qquad \varepsilon_{11}^{T} - \varepsilon_{11}^{S} = e_{15}^{2}\, s_{44}^{E}$$
$$\varepsilon_{33}^{T} - \varepsilon_{33}^{S} = 2e_{31}^{2}(s_{11}^{E} + s_{12}^{E}) + 4e_{31}e_{33}\, s_{13}^{E} + e_{33}^{2} s_{33}^{E}$$

One might well ask 'Why constitutive equations?' The answer is simply '10^{23} !' The relatively few material constants in the equations of Table III stand in for the interactions between an enormous number of atoms. The simplification is astounding, but it is not simple!

TABLE IV. Piezoelectric coefficients

Coefficient	Abbreviation	Units
Stress Constant	e	C/m^2
Strain Coefficient	d	m/V = C/N
Stress Modulus	h	N/C = V/m
Strain Constant	g	m^2/C
Polarization Modulus	a	N/C = V/m
Polarization Constant	b	m^2/C

We are told that there are but four basic interactions (forces) in nature: 1) weak interactions between leptons, baryons, and mesons; these are responsible, e.g., for neutron decay/radioactivity (H Becquerel again!); but these are of very short range, < few fm. 2) strong interactions between hadrons (baryons and mesons); again of very short range, < few fm. 3) gravitational interactions [3]; long range, inverse-square, but very, very weak compared to: 4) electromagnetic interactions which are of long range and affect primarily charged particles. The electrical and mechanical (elastic) forces in the constitutive equations are electromagnetic. Yet Coulomb's force law [3], is inverse-square between particles. Why are both Hooke's (elastic) law and the piezoelectric equation linear? The answer here is deep. It is the massive cancellations that take place among the '10^{23}' particles that render the equations (to a first approximation) linear. By sheer coincidence, the bound motion of two classical particles mutually subject to a central force law possesses closed (elliptical) orbits only for the exceptional cases of Hookean (linear) and Coulombic (inverse-square) attraction.

COUPLING COEFFICIENTS

More important by far than the piezoelectric coefficients are the dimensionless combinations of material parameters called piezocoupling coefficients. These are listed in Table V, and arise from the particular forms of the constitutive equations used. Table VI gives some of their applications.

TABLE V. Piezoelectric coupling coefficients, k

$k^2_{hom} = d^2/(\varepsilon^T s^E) = h^2/(\beta^S c^D) = e^2/(\varepsilon^T c^E) = e^2/(\varepsilon^S c^D) = g^2/(\beta^T s^E) = g^2/(\beta^S s^D)$

$k^2_{mix} = e^2/(\varepsilon^S c^E) = g^2/(\beta^T s^D) = d^2/(\varepsilon^S s^E) = d^2/(\varepsilon^T s^D) = h^2/(\beta^S c^E) = h^2/(\beta^T c^D)$

TABLE VI. Why coupling coefficients ?

Component/Device	Parameter
Transducers; Filters	Bandwidth; Insertion loss
Resonators; Resonant MEMS	Pole-Zero spacing
Actuators; Sensors	Elec-mech conversion efficiency

PIEZOELECTRIC CYCLES

One may see the importance of coupling factors in yet another way. By constructing the piezo equivalent of a thermodynamic cycle, the interchange of energies may be traced. A simple cycle is shown in Fig. 3, wherein it is seen that the intermediate values are functions of k.

NEUMANN'S PRINCIPLE

Franz Neumann [21] established a fundamental principle governing the physical behavior of crystalline materials [1, 36, 37, 43]. It was named "Neumann's Principle" by his student, Voigt [18]. It may be stated in several equivalent forms:

- The symmetry elements of any physical property of a crystal must include all the symmetry elements of the point group of the crystal.

- Every physical property of a crystal must possess at least the symmetry of the point group of the crystal.

- Any kind of symmetry that is possessed by the crystallographic form of a material is possessed by the material in respect of every physical property.

INDEPENDENT CONSTANTS

The crystallographic point groups determine the forms of the elastic, piezoelectric, and dielectric matrices (and those of other effects represented in phenomenological form). The numbers of independent constants for the piezoelectric groups are given in Tables VIIa and VIIb. Figure 4 gives the explicit forms for the piezoelectric 'e' matrices for all classes.