Elastic, Piezoelectric, and Dielectric Constants of Polarized Barium Titanate Ceramics and Some Applications of the Piezoelectric Equations

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A complete set of the elastic, piezoelectric, and dielectric constants of polarized barium titanate ceramics is presented. The various electromechanical coupling factors, as derived from the piezoelectric equations, and their numerical values are also given. The determination of the elastic and piezoelectric constants using the resonant method applied to small bars, square plates, and disks is discussed.

I. INTRODUCTION

NO complete set of the elastic, piezoelectric, and dielectric constants for polarized barium titanate ceramics has been published. The values of polarized barium titanate ceramics are to some extent dependent on its processing and on the electric field applied. Unpolarized barium titanate cermaics are isotropic. Under the influence of an applied electric field, the structure reduces to two-dimensional isotropy in the plane normal to the direction of polarization; in regard to all those physical properties that are described by tensors of ranks up to four and which include dielectric, piezoelectric, and elastic phenomena, the symmetry type associated with the crystallographic class C_{6v} implies two-dimensional isotropy. If the Z-axis is taken as the symmetry axis, this crystal class is defined by five elastic moduli (stiffnesses), $c_{11}=c_{22}$, c_{33}, c_{12}, $c_{13}=c_{23}$, $c_{44}=c_{55}$, $c_{66}=\frac{1}{2}(c_{11}-c_{12})$; by three piezoelectric moduli (stress constants), $e_{15}=e_{24}$, $e_{31}=e_{32}$, e_{33}; and by two permittivities, $\epsilon_{11}=\epsilon_{22}$, ϵ_{33}. The schemes for s_{ik}, d_{ik}, and β_{ik} are identical with the corresponding schemes above. The plane perpendicular to the Z-axis fulfills isotropic conditions.

In a recent paper[1] two-dimensional applications of the piezoelectric equations of state were considered, and some planar elastic and piezoelectric constants were introduced. Polarized barium titanate ceramics, having high values of the piezoelectric and dielectric constants, are particularly suitable to illustrate the differences between the various constants related to different boundary conditions.

II. ELASTIC, PIEZOELECTRIC, AND DIELECTRIC CONSTANTS OF BARIUM TITANATE

Numerical values for barium titanate ceramics are known[2,3] for the elastic compliances s_{11}^E and s_{12}^E; hence Poisson's ratio in the plane perpendicular to Z, $\sigma=\sigma_{12}^E=-s_{12}^E/s_{11}^E$, $s_{66}=2(s_{11}^E-s_{12}^E)$. These values are obtained from frequency measurements of extensional modes of bars and contour modes of disks of orientation Z. In addition, c_{33}^D and $c_{44}^D=1/s_{44}^D$ are obtained from thickness extensional modes of thin Z-plates and thickness shear modes of X-plates, respectively. s_{44}^D is obtained from bars of orientation XZ. In order to determine the full set of elastic constants, more measurements are required. Values for the three piezoelectric coefficients d_{ik} and the two permittivities ϵ_{ik} at constant stress are also known. A typical value for density is $5.72\cdot10^3$kg m^{-3}.

Using the pulse method, Huntington and Southwick[4] determined the velocities of longitudinal and transverse waves in the directions parallel to the edges of a polarized cube of barium titanate ceramic. This leads to the values for c_{11}^E, c_{44}^E, c_{66}, c_{33}^D, and c_{44}^D. In the following a full set of the elastic, piezoelectric, and dielectric constants for the various boundary conditions is evaluated from Huntington's observed values of c_{11}^E and c_{44}^E, the ratio $s_{33}^E/s_{11}^E=1.045$ observed by Moseley[5] for maximum-poled material, and from the values given in references 2, 3, and including new measurements by D. Berlincourt and H. Krueger.[6] Table I gives the resulting typical values of the elastic compliances s_{ik} and elastic stiffnesses c_{ik} for constant electric field and constant displacement; Table II gives typical values of the two kinds of piezoelectric strain constants d_{ik} and g_{ik} and the stress constants e_{ik} and h_{ik}; Table III the permittivities ϵ_{ik} at constant stress and constant strain. All values are expressed in mks units and refer to a temperature of 25°C. As already mentioned, the values depend to some extent on the poling and aging.

The general relationships between the various constants can be found in the Institute of Radio Engineers Standards[7] on Piezoelectric Crystals, 1949, and are easily simplified for the crystal class considered.

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[1] R. Bechmann, Inst. Radio Engrs. Trans. Ultras. Eng. 3, 43–62 (1955).
[2] H. Jaffe, *Electromechanical Properties of Titanate Ceramics, Brush Strokes* (The Brush Development Company, Cleveland, Ohio, December, 1951), pp. 1–7.
[3] D. Berlincourt, "Recent developments in ferroelectric transducer materials," Proc. Natl. Electronics Conference, Chicago (October 5, 1955).
[4] H. B. Huntington and R. D. Southwick, J. Acoust. Soc. Am. 27, 677–679 (1955).
[5] D. S. Moseley, J. Acoust. Soc. Am. 27, 947–950 (1955).
[6] D. Berlincourt and H. Krueger, "Measurements of elastic and piezoelectric constants of barium titanate ceramics," Contract No. Nonr-1055(00), Technical Report No. 10 (1956), also partly given in reference 3.
[7] Proc. Inst. Radio Engrs. 37, 1378–1395 (1949).

TABLE I. Typical values (in mks units) of elastic coefficients (elastic compliances) s_{ik} and elastic moduli (elastic stiffness) c_{ik}.

$s_{11}^E=8.55\cdot 10^{-12}m^2N^{-1}$	$s_{11}^D=8.18\cdot 10^{-12}m^2N^{-1}$
$s_{33}^E=8.93$	$s_{33}^D=6.76$
$s_{12}^E=-2.61$	$s_{12}^D=-2.98$
$s_{13}^E=-2.85$	$s_{13}^D=-1.95$
$s_{44}^E=23.3$	$s_{44}^D=18.3$
$s_{66}^E=22.3$	$s_{66}^D=s_{66}^E=s_{66}$
$c_{11}^E=166\cdot 10^9Nm^{-2}$	$c_{11}^D=168\cdot 10^9Nm^{-2}$
$c_{33}^E=162$	$c_{33}^D=189$
$c_{12}^E=76.6$	$c_{12}^D=78.2$
$c_{13}^E=77.5$	$c_{13}^D=71.0$
$c_{44}^E=42.9$	$c_{44}^D=54.6$
$c_{66}^E=44.8$	$c_{66}^D=c_{66}^E=c_{66}$

III. PLANAR ELASTIC AND PIEZOELECTRIC MODULI

In an earlier paper[8] the notation $\bar{c}_{ik}(i,k=1,2,6)$ for the planar elastic stiffnesses has been used referring to a plane perpendicular to the Z-axis.[9] The corresponding planar piezoelectric stress coefficients have been introduced by $\bar{e}_{3k}$ and $\bar{h}_{3k}$ $(k=1,2,6)$. For the crystal class C_{6v},

$$\bar{c}_{11}=\bar{c}_{22}=\frac{s_{11}}{s_{11}^2-s_{12}^2},\quad \bar{c}_{12}=\frac{-s_{12}}{s_{11}^2-s_{12}^2},$$

$$\bar{c}_{66}=\tfrac{1}{2}(\bar{c}_{11}-\bar{c}_{12})=\frac{1}{2(s_{11}-s_{12})}=c_{66},\quad \bar{c}_{16}=\bar{c}_{26}=0 \tag{1}$$

and

$$\bar{c}_{11}\pm\bar{c}_{12}=\frac{1}{s_{11}\pm s_{12}}.$$

Further

$$\bar{e}_{21}=\bar{e}_{32}=d_{31}(\bar{c}_{11}^E+\bar{c}_{12}^E)=\frac{d_{31}}{s_{11}^E+s_{12}^E},\quad \bar{e}_{36}=0$$

$$\bar{h}_{31}=\bar{h}_{32}=g_{31}(\bar{c}_{11}^D+\bar{c}_{12}^D)=\frac{g_{31}}{s_{11}^D+s_{12}^D},\quad \bar{h}_{36}=0. \tag{2}$$

The dielectric constant, $\epsilon_{33}^{(S)}$, at constant planar strain is defined by

$$\epsilon_{33}^T-\epsilon_{33}^{(S)}=2\bar{e}_{31}d_{31}=\frac{2d_{31}^2}{s_{11}^E+s_{12}^E}=\frac{2\bar{e}_{31}^2}{\bar{c}_{11}^E+\bar{c}_{12}^E}. \tag{3}$$

Using the values of Table I, it follows:

$$\bar{c}_{11}^E=129\cdot 10^9Nm^{-2}\qquad \bar{c}_{11}^D=141\cdot 10^9Nm^{-2}$$
$$\bar{c}_{12}^E=39.4\qquad \bar{c}_{12}^D=51.4.$$
$$\bar{c}_{66}=c_{66}=44.8$$

From Table II are obtained the values:

$$\bar{e}_{31}=-13.3Cm^{-2}\qquad \bar{h}_{31}=-7.91\cdot 10^8VC^{-1}.$$

The values of Table III give

$$\epsilon_{33}^{(S)}=1470\cdot 10^{-11}Fm^{-1}.$$

[8] See reference 1, Sec. I.

[9] These stiffnesses have been originally introduced by Voigt as γ_{ik}. W. Voigt, *Lehrbuch der Kristallphysik* (Teubner, Leipzig, 1928), second edition.

The difference between ϵ^T and ϵ^S is given by

$$\epsilon_{33}^T-\epsilon_{33}^S=2e_{31}d_{31}+e_{33}d_{33}=(69+355)\cdot 10^{-11}$$
$$=424\cdot 10^{-11}Fm^{-1}. \tag{4}$$

This expression can be written in the form[10]

$$\epsilon_{33}^T-\epsilon_{33}^S=\frac{2d_{31}^2}{s_{11}^E+s_{12}^E}+\frac{e_{33}^2}{c_{33}^E}$$
$$=(210+214)\cdot 10^{-11}=424\cdot 10^{-11}Fm^{-1}. \tag{5}$$

According to Eq. (3) the term $2d_{31}^2/(s_{11}^E+s_{12}^E)$ of Eq. (5) represents $\epsilon_{33}^T-\epsilon_{33}^{(S)}$. The dielectric constant $\epsilon_{33}^{(S)}$ determines in first approximation the shunt capacitance of the equivalent electric circuit of the planar modes of vibration.

IV. VARIOUS ELECTROMECHANICAL COUPLING FACTORS

According to the choice of the independent and dependent variables in the piezoelectric equations of state, various electromechanical coupling factors can be defined. The coupling factors and their numerical values for barium titanate, calculated from Tables I to III are: for homogeneous variables in the equation of state, where T, the stress, and E, the electric field, are taken as independent variables, S, the strain, and D, the electric displacement, as dependent variables, or vice versa:

$$(k_{15})_{\text{hom}}=\frac{d_{15}}{(\epsilon_{11}^Ts_{55}^E)^{\frac{1}{2}}}=\frac{h_{15}}{(\beta_{11}^Sc_{55}^D)^{\frac{1}{2}}}=0.476,$$

$$(k_{31})_{\text{hom}}=\frac{d_{31}}{(\epsilon_{33}^Ts_{11}^E)^{\frac{1}{2}}}=0.208, \tag{6}$$

$$(k_{33})_{\text{hom}}=\frac{d_{33}}{(\epsilon_{33}^Ts_{33}^E)^{\frac{1}{2}}}=0.493.$$

The coupling factors for mixed variables in the equation of state where S and E are taken as independent variables, T and D as dependent variables, or vice versa, are

$$(k_{15})_{\text{mix}}=\frac{e_{15}}{(\epsilon_{11}^Sc_{55}^E)^{\frac{1}{2}}}=\frac{g_{15}}{(\beta_{11}^Ts_{55}^D)^{\frac{1}{2}}}=0.527,$$

$$(k_{33})_{\text{mix}}=\frac{e_{33}}{(\epsilon_{33}^Sc_{33}^E)^{\frac{1}{2}}}=0.414. \tag{7}$$

Of practical interest is the planar coupling factor k_p for the stress system $T_1=T_2$. The homogenous type is defined by

$$(k_p)_{\text{hom}}=\frac{\sqrt{2}d_{31}}{(\epsilon_{33}^T(s_{11}^E+s_{12}^E))^{\frac{1}{2}}}=0.354, \tag{8}$$

[10] See reference 1, Sec. I.

and the mixed type by

$$(k_p)_{\mathrm{mix}}=\frac{\sqrt{2}d_{31}}{(\epsilon_{33}^{(S)}(s_{11}^E+s_{12}^E))^{\frac{1}{2}}}$$

$$=\frac{\sqrt{2}\bar{e}_{31}}{(\epsilon_{33}^{(S)}(\bar{c}_{11}^E+\bar{c}_{12}^E))^{\frac{1}{2}}}=0.378.$$

Between the homogeneous and mixed coupling coefficients of k_{15} in Eqs. (6) and (7) and k_p in Eq. (8),

$$k_{\mathrm{hom}}^2-k_{\mathrm{mix}}^2+k_{\mathrm{hom}}^2k_{\mathrm{mix}}^2=0 \quad (9)$$

and consequently,

$$k_{\mathrm{hom}}^2=\frac{k_{\mathrm{mix}}^2}{1+k_{\mathrm{mix}}^2} \quad \text{or} \quad k_{\mathrm{mix}}^2=\frac{k_{\mathrm{hom}}^2}{1-k_{\mathrm{hom}}^2}. \quad (10)$$

The consideration of the coupling factors in this section is of interest as the elastic, piezoelectric, and dielectric properties are often expressed in terms of coupling factors.

V. ELASTIC CONSTANTS DETERMINED BY THE RESONANT METHOD

The elastic compliances s_{11}^E, s_{12}^E, and s_{66} and Poisson's ratio σ can be determined from measurement of the series resonance frequency f_s of piezoelectrically excited length extensional modes of small bars and contour extensional modes of square and circular plates perpendicular to Z. The samples are fully plated.

From measurement of the frequency of the length extensional mode of a small bar of orientation ZX and length l, the elastic compliance s_{11}^E can be determined according to the equation:

$$s_{11}^E=1/4\rho N^2, \quad (11)$$

where $N=f_s\cdot l$ is the frequency constant and ρ is the density.

To determine s_{12}^E or Poisson's ratio σ, two-dimensional modes of plates are necessary. Suitable modes are the contour extensional mode of a disk or the contour extensional modes of a square plate. For isotropic conditions and $d_{31}=d_{32}$, two kinds of contour extensional modes of square plates are excitable: the well-known mode III[11–13] and a mode recently described by H. Baerwald.[14] For the present purpose this mode is designated as mode IV of square plates.

The frequency constant for the fundamental mode and the overtones of a thin disk is given by[15]

$$N_d=\frac{\kappa}{\pi}\left(\frac{\bar{c}_{11}}{\rho}\right)^{\frac{1}{2}}=\frac{\kappa}{\pi}\left(\frac{1}{\rho s_{11}(1-\sigma^2)}\right)^{\frac{1}{2}}, \quad (12)$$

where κ is root of the equation,

$$\kappa J_0(\kappa)-(1-\sigma)J_1(\kappa)=0, \quad (13)$$

and $J_0(\kappa)$ and $J_1(\kappa)$ are the Bessel functions of the orders zero and one. In the vicinity of $\sigma=0.30$, the first root is approximately[16]

$$\kappa_1=2.04885+0.62324(\sigma-0.30)-0.202(\sigma-0.30)^2. \quad (14)$$

The higher roots for $\sigma=0.30$ are: $\kappa_2=5.39$, $\kappa_3=7.57$, $\kappa_4=11.73$ and for $n>4$, $\kappa_n\rightarrow(n+\frac{1}{4})\pi$. From the measurement of the frequency constant of one of the three modes mentioned before:

$$s_{11}^E=F^2/4\rho N^2, \quad (15)$$

where for the disk $N=f_s\cdot\phi$ and $F=F_d$, (ϕ is the diameter of the disk). Similarly for modes III and IV in Eq. (15), N and F refer to N_{III}, F_{III} and N_{IV}, F_{IV}, respectively. The values of F as a function of σ for the three modes are given in Table IV. The values of F_{III} and F_{IV} are taken from reference 14. The values of F in Table IV are applicable to sufficiently thin plates. In case of larger thickness-diameter ratio a thickness correction is necessary and is given for mode III and IV in reference 14. From the measurement of the longitudinal modes of bars and of the modes of plates, s_{11} and σ can be determined. As the frequency constant of mode IV strongly depends on σ, the measurements of both modes III and IV of the same plate lead also to a determination of s_{11} and σ. However, the accuracy of the determination of σ is higher. Furthermore, s_{11} and σ can be determined from the same plate. This eliminates

TABLE II. Typical values (in mks units) of piezoelectric coefficients (piezoelectric strain constants) d_{ik}; piezoelectric strain constants g_{ik}; piezoelectric moduli (piezoelectric stress constants) e_{ik}; piezoelectric stress constants h_{ik}.

$d_{15}=270\cdot10^{-12}CN^{-1}$	$e_{15}=11.6Cm^{-2}$
$d_{31}=-79$	$e_{31}=-4.4$
$d_{33}=191$	$e_{33}=18.6$
$g_{15}=18.8\cdot10^{-3}m^2C^{-1}$	$h_{15}=10.3\cdot10^2NC^{-1}$
$g_{31}=-4.7$	$h_{31}=-3.5$
$g_{33}=11.4$	$h_{33}=14.8$

TABLE III. Typical values (in mks units) of dielectric constants (permittivities) ϵ_{ik}.

$\epsilon_{11}^T=1436\cdot10^{-11}Fm^{-1}$	$\epsilon_{11}^S=1123\cdot10^{-11}Fm^{-1}$
$\epsilon_{33}^T=1680$	$\epsilon_{33}^S=1256$

[11] H. Ekstein, Phys. Rev. 66, 108–118 (1944).
[12] H. Mähly, Helv. Phys. Acta 18, 248–251 (1945).
[13] R. Bechmann, "Contour modes of plates excited piezoelectrically and determination of elastic and piezoelectric coefficients," Inst. Radio Engrs. Convention Record, National convention, Vol. 2, Part 6—Audio and Ultrasonics, 77–85 (1954).
[14] H. G. Baerwald and C. Libove, "Breathing vibrations of planarly isotropic square plates," Contract No. Nonr-1055(00), Technical Report No. 8 (December 12, 1955).
[15] W. P. Mason and H. Jaffe, Proc. Inst. Radio Engrs. 42, 921–930 (1954).
[16] H. G. Baerwald, "Electrical admittance of a circular ferroelectric disc," Contract No. Nonr-1055(00), Technical Report No. 3 (January 19, 1955).

TABLE IV. The constants κ_1 and F as function of σ (F_{III} and F_{IV} according to H. G. Baerwald and C. Libove).

σ	κ_1	F_d	F_{III}	F_{IV}	$F_{\mathrm{IV}}/F_{\mathrm{III}}$
0.250	2.0172	1.3272	1.1218	1.7012	1.5164
0.260	2.0236	1.3348	1.1277	1.6974	1.5052
0.270	2.0300	1.3422	1.1336	1.6938	1.4942
0.280	2.0362	1.3503	1.1396	1.6903	1.4832
0.290	2.0425	1.3587	1.1458	1.6869	1.4729
0.300	2.0488	1.3673	1.1519	1.6836	1.4615
0.310	2.0551	1.3761	1.1582	1.6804	1.4508
0.320	2.0612	1.3851	1.1646	1.6773	1.4403
0.330	2.0673	1.3943	1.1710	1.6744	1.4299
0.340	2.0735	1.4037	1.1775	1.6716	1.4197
0.350	2.0795	1.4132	1.1841	1.6690	1.4096

TABLE V. The constants β as function of σ (β_{III} and β_{IV} according to H. G. Baerwald and C. Libove).

σ	β_d	β_{III}	β_{IV}
0.250	4.8254	6.38	0.058
0.260	4.8287	6.37	0.066
0.270	4.8380	6.36	0.075
0.280	4.8376	6.35	0.085
0.290	4.8366	6.34	0.096
0.300	4.8347	6.32	0.107
0.310	4.8323	6.31	0.121
0.320	4.8312	6.29	0.135
0.330	4.8285	6.27	0.151
0.340	4.8280	6.25	0.168
0.350	4.8271	6.23	0.186

any differences caused by using two different specimens. The ratio of the frequencies of modes III and IV,

$$f_{\mathrm{IV}}/f_{\mathrm{III}}=F_{\mathrm{IV}}/F_{\mathrm{III}}, \tag{16}$$

gives directly Poisson's ratio. The ratio $F_{\mathrm{IV}}/F_{\mathrm{III}}$ as a function of σ is also shown in Table IV.

From measurements of higher order frequencies of small bars XZ, $s_{44}{}^D=s_{55}{}^D$ can be obtained from equation:

$$s_{44}{}^D=n^2/4\rho N_n{}^2, \tag{17}$$

where $N_n=f_n\cdot b$, and b is the dimension in the direction of the X-axis. The elastic compliance $s_{33}{}^D$ can be obtained from measurements on small bars parallel to the Z-axis excited by the field parallel to the length direction.

VI. PIEZOELECTRIC CONSTANTS DETERMINED BY THE RESONANT METHOD

The determination of piezoelectric constant d_{31} using the contour extensional mode of a bar, contour extensional mode of a disk or square plate (mode III), has already been discussed in detail.[17] For the modes considered, the piezoelectric constant d_{31} can be determined by measurement of the frequency constant and the separation of the resonant and antiresonant frequencies, $1/r=f_a{}^2/f_r{}^2-1$, from the expression

$$d_{31}=\pm\frac{1}{N}\left(\frac{p}{\rho\beta}\frac{\epsilon_{33}{}^T}{1+pr\chi}\right)^{\frac{1}{2}}. \tag{18}$$

For the fundamental extensional mode of a bar,

$$\beta=32/\pi^2 \quad\text{and}\quad p=8/\pi^2;$$

for the fundamental mode of a disk,

$$\beta_d=\frac{4\pi^2}{\kappa_1{}^2}\frac{(1+\sigma)^2}{\kappa_1{}^2-1+\sigma^2}$$

and

$$p=\frac{2(1+\sigma)}{\kappa_1{}^2-1+\sigma^2};$$

for the contour extensional mode III of a square plate and for very small σ, $\beta_{\mathrm{III}}=64/\pi^2$ and $p=8/\pi^2$. The values of β_d, β_{III}, and β_{IV} for σ in the range 0.250–0.350 are listed in Table V. The values of β refer to fully plated samples. The factor χ in Eq. (18) takes into account the influence of the other modes of the specimen excitable with the same electrode arrangement. For specimens with a single series of modes, as fulfilled for thin bars and disks, $\chi\approx 1$, values of 0.98 have been observed (see reference 13). As the excitation of mode IV is rather weak, following from the small values of β_{IV} listed in Table V, its influence on mode III of the square plate can be neglected. In Eq. (18) $\epsilon_{33}{}^T$ is the dielectric constant at constant stress which can be measured directly at a very low frequency. The agreement of the results of d_{31} obtained from the three different modes mentioned is usually very satisfactory.

The piezoelectric constant d_{15} can be determined from measurement of resonant and antiresonant frequencies of higher overtones of small bars of orientation XZ according to the equation:

$$d_{15}=\pm\frac{1}{N_n}\left(\frac{p_n}{\rho\beta_n}\frac{\epsilon_{11}{}^T}{1+p_nr}\right)^{\frac{1}{2}}, \tag{19}$$

where for the nth overtone $\beta_n=32/n^4\pi^2$ and $p=8/\pi^2n^2$. The frequency constant N_n is defined by $f_n\cdot b$, where b is the dimension in the direction of the X-axis.

The piezoelectric constant d_{33} can be determined from length extensional mode of small bars excited in its length direction.

Some details of methods for measuring piezoelectric, elastic, and dielectric coefficients of crystals and ceramics can be found in a paper by W. P. Mason and H. Jaffe.[18]

[17] See reference 13, Sec. V.

[18] See reference 15, Sec. V.