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Elastic and Piezoelectric Coefficients of Single-Crystal Barium Titanate*

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Mechanical resonance and antiresonance frequencies were measured on barium titanate single-crystal elements maintained under electric dc bias from −50°C to +150°C. A complete set of elastic, piezoelectric, and dielectric constants of the tetragonal modification at 25°C is obtained. The elastic compliances show substantial deviation from cubic symmetry. Measurements in the orthorhombic state show longitudinal compliance four times higher than in the tetragonal state.

INTRODUCTION

KNOWLEDGE of the elastic constants of single-crystal barium titanate is required for any quantitative theory of ferroelectricity in this material. An early partial set of elastic constants at room temperature was given by Bond, Mason, and McSkimin.[1] They found nearly cubic symmetry for the open-circuit elastic constants c^D. This may, however, have been due to incomplete domain alignment, which is also indicated by a free permittivity $\epsilon_{33}{}^T$ more than ten times that now generally found for good single-domain crystals.[2] Devonshire[3] used power expansion of the free energy to derive a complete set of elastic, dielectric, and piezoelectric constants from the c^D values of Bond *et al.*, from crystal axial ratios of Kay and Vousden,[4] and from permittivities ϵ^T and spontaneous polarization of Merz.[2] More recently Huibregtse, Drougard, and Young[5] gave a partial set of compliances, measured on high quality crystals, as functions of temperature.

In the following, we give complete sets of elastic constants for the tetragonal crystal at 25°C and the cubic crystal at 150°C. Measurements were made under closely controlled conditions on selected crystals grown by the Remeika[6] method. Resonances were also obtained in the orthorhombic state which is stable below about 10°C, but since twinning at the transformation point cannot be avoided, our data on the orthorhombic crystal do not refer to a true single crystal.

A complete set of piezoelectric constants for the tetragonal crystal at 25°C and partial piezoelectric data for orthorhombic crystals are also given.

MEASUREMENT METHODS

The elastic and piezoelectric constants of tetragonal crystals were determined from resonance and antiresonance measurements. Bars and plates were cut with an abrasive wire saw from carefully selected portions of barium titanate crystals. All measurements except those in thickness shear were made with a maintained electric bias field of 10 kv/cm. All test specimens were first poled at 10 kv/cm while being cooled from 120 to 50°C. (The term "to pole" describes the process of imparting remanent polarization to multidomain ferroelectric crystal or ceramic by treatment in a dc electric field.) This poling treatment was found necessary, since otherwise the maintained 10 kv/cm bias field was not always sufficient to remove all 90° and 180° twinning.

The elastic compliance $s_{11}{}^E$ was obtained from resonance frequencies of bars elongated in the [100] direction with thickness along [001] [Fig. 1(a)], using the relationship

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

where ρ = density in kg/m³ and N_R = resonance frequency constant in cycle meters/second.

The elastic compliance $s_{12}{}^E$ was obtained from $s_{11}{}^E$ above and the resonance frequencies of square plates oriented with sides along [010] and [100] [Fig. 1(c)]. The frequency constant for the extensional "breathing" mode of a square plate was given by Ekstein[7] as follows:

$$N_R{}^2 = \frac{1}{4\rho(s_{11}+s_{12})}\left[1+\left(1-\frac{8}{\pi^2}\right)\left(\frac{s_{12}}{s_{11}+s_{12}}\right)\right]. \tag{2}$$

An isolated mode is obtained with barium titanate, since his conditions, $s_{11}=s_{22}$ and $s_{16}=s_{26}=0$, are met.

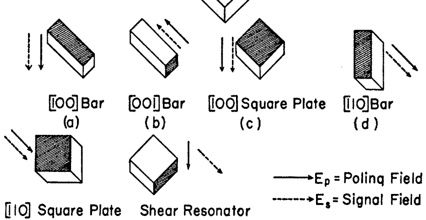

FIG. 1. Barium titanate crystal plate, showing orientation of test specimens for resonance measurements.

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* Supported in part by the Office of Naval Research.

[1] Bond, Mason, and McSkimin, Phys. Rev. **82**, 442 (1951).

[2] W. J. Merz, Phys. Rev. **76**, 1221 (1949).

[3] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949); **42**, 1065 (1951).

[4] H. F. Kay and P. Vousden, Phil. Mag. **40**, 1019 (1949).

[5] Huibregtse, Drougard, and Young, Phys. Rev. **98**, 1562(A) (1955). Curves were reproduced by W. Känzig in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 50.

[6] J. P. Remeika, J. Am. Chem. Soc. **76**, 940 (1954).

[7] H. Ekstein, Phys. Rev. **66**, 108 (1944).

TABLE I. Measured frequency constants at 25°C.

Specimen	Mode	Cycle meters/second N_A	N_R	N_A/n
[100] bar	Transverse expander	2365	2275	
[110] bar	Transverse expander	3060	2862	
[100] square plate	"Breathing" extensional	2920	2640	
[110] square plate	"Breathing" extensional	2940	2690	
[100] square plate	Thickness expansion fundamental	2710	2360	
[100] square plate	Thickness expansion 3rd harmonic	8170	···	2723
[100] plate (side-electroded)	Thickness shear fundamental	2090	1805	
[100] plate (side-electroded)	Thickness shear 3rd harmonic	5510	···	1837
[001] bar	Longitudinal expander	1960	1670	

To obtain the shear compliance s_{66}, an elastic compliance $s_{11}'^{E}$ was determined from the resonance frequency constants of bars oriented with length along [110] [Fig. 1(d)]. In terms of unrotated compliances,

$$s_{11}'=\tfrac{1}{2}s_{11}+\tfrac{1}{2}s_{12}+\tfrac{1}{4}s_{66}. \quad (3)$$

The stiffness c_{33}^{D} was determined from overtones of the antiresonance frequencies of square plates with thickness along [001] [Figs. 1(c) and 1(e)],

$$c_{33}^{D}=4\rho N_A^2/n^2, \quad (4)$$

where n = order of harmonic and N_A = antiresonance frequency constant.

TABLE II. Elastic, piezoelectric, and dielectric coefficients at 25°C.[a]

	Crystal	Ceramic	Devonshire crystal values
s_{11}^{E}	8.05	8.55	11.2
s_{33}^{E}	15.7	8.93	23.2
s_{12}^{E}	−2.35	−2.61	−1.3
s_{13}^{E}	−5.24	−2.85	−8.2
s_{44}^{E}	18.4	23.3	54
s_{66}	8.84	22.3	8.1
s_{11}^{D}	7.25	8.18	
s_{33}^{D}	10.8	6.76	
s_{12}^{D}	−3.15	−2.98	
s_{13}^{D}	−3.26	−1.95	
s_{44}^{D}	12.4	18.3	
$\epsilon_{11}^{T}/\epsilon_0$	2920	1436	4000
$\epsilon_{33}^{T}/\epsilon_0$	168	1680	225
$\epsilon_{11}^{S}/\epsilon_0$	1970	1123	600
$\epsilon_{33}^{S}/\epsilon_0$	111 calc 109 meas.	1256	90
d_{15}	392	270	1160
d_{31}	−34.5	−79	−63
d_{33}	85.6	191	165
g_{15}	15.2	18.8	
g_{31}	−23.0	−4.7	
g_{33}	57.5	11.4	
k_{31}	0.315	0.208	
k_{33}	0.560	0.494	
k_{15}	0.570	0.466	

[a] s in 10^{-12} m²/n; d in 10^{-12} coul/n; g in 10^{-3} volt m/n. We use mks units; 1 n = 1 newton = 10^5 dynes. 1 coul/n = 1 volt/m = 3×10^4 esu.

The fundamental antiresonance frequencies of [001] bars [Fig. 1(b)] were measured to obtain s_{33}^{D}. In this case, the c direction was oriented along the length of crystal bar by the poling process. This introduces some strains in the crystal, since most domains are oriented with c parallel to the thickness of the crystal plate as grown. The antiresonance frequency constant for this case gives

$$s_{33}^{D}=1/(4\rho N_A^2). \quad (5)$$

The shear compliance s_{44}^{D} was obtained from overtones of the antiresonance frequencies of plates with thickness along c, but electrodes on edges perpendicular to an a axis [Fig. 1(f)]. Test plates were first poled to eliminate domain twinning; the poling electrodes were then removed and new electrodes were placed on opposite edges perpendicular to a. The equation for this case is

$$s_{44}^{D}=\frac{1}{(4\rho N_A^2/n^2)}. \quad (6)$$

The coupling coefficient k_{31} was obtained from the resonance and antiresonance frequencies of [100] bars [Fig. 1(a)] by using the relationship[8]

$$\frac{k_{31}^2}{1-k_{31}^2}=\frac{\pi}{2}\frac{F_A}{F_R}\tan\left(\frac{\pi}{2}\frac{\Delta F}{F_R}\right), \quad \text{where} \quad \Delta F=F_A-F_R. \quad (7)$$

The coupling coefficient k_{33} was obtained from the resonance and antiresonance frequencies of [001] bars by using the relationship

$$k_{33}^2=\frac{\pi}{2}\frac{F_R}{F_A}\tan\left(\frac{\pi}{2}\frac{\Delta F}{F_A}\right). \quad (8)$$

The shear coupling coefficient k_{15} was determined from a measurement of the free and clamped capacitances of plates with thickness along c and electrodes on edges perpendicular to an a axis [Fig. 1(f)] by using the relationship

$$\epsilon_{11}^{S}=\epsilon_{11}^{T}(1-k_{15}^2). \quad (9)$$

The constant-field compliances s_{33}^{E} and s_{44}^{E} were determined from s_{33}^{D} and s_{44}^{D}, respectively, as follows:

$$s_{33}^{E}=s_{33}^{D}/(1-k_{33}^2); \quad (10)$$

$$s_{44}^{E}=s_{44}^{D}/(1-k_{15}^2). \quad (11)$$

The constant-charge density compliances s_{11}^{D} and s_{12}^{D} were obtained from s_{11}^{E} and s_{12}^{E} by the relations[9]

$$s_{11}^{D}=(1-k_{31}^2)s_{11}^{E}; \quad (12)$$

$$s_{12}^{D}=s_{12}^{E}-k_{31}^2 s_{11}^{E}. \quad (13)$$

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[8] W. P. Mason, *Piezoelectric Crystals and their Application to Ultrasonics* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), p. 66.

[9] The relationships (13), (20), and (21) are derived in the appendix.

The piezoelectric constants were determined from the respective coupling coefficients, compliances, and permittivities as follows:

$$g_{31}=k_{31}(s_{11}{}^{E}/\epsilon_{33}{}^{T})^{\frac{1}{2}}, \tag{14}$$

$$g_{33}=k_{33}(s_{33}{}^{E}/\epsilon_{33}{}^{T})^{\frac{1}{2}}, \tag{15}$$

$$g_{15}=k_{15}(s_{44}{}^{E}/\epsilon_{11}{}^{T})^{\frac{1}{2}}, \tag{16}$$

$$d_{31}=\epsilon_{33}{}^{T}g_{31}, \tag{17}$$

$$d_{33}=\epsilon_{33}{}^{T}g_{33}, \tag{18}$$

$$d_{15}=\epsilon_{11}{}^{T}g_{15}. \tag{19}$$

For both constant-field and constant-charge density conditions, all values in the s matrix except s_{13} have now been determined, and in addition $c_{33}{}^{D}$ is known. From the constant-charge density matrix and $c_{33}{}^{D}$, a value for $s_{13}{}^{D}$ was calculated. $s_{13}{}^{E}$ was then obtained by[9]

$$s_{13}{}^{E}=s_{13}{}^{D}+g_{33}d_{31}. \tag{20}$$

The clamped permittivity $\epsilon_{33}{}^{S}$ was measured directly, and was in addition derived from the free permittivity $\epsilon_{33}{}^{T}$, the piezoelectric constants d_{31} and d_{33}, and the elastic compliances $s_{13}{}^{E}$, $s_{33}{}^{E}$, $s_{11}{}^{E}$, and $s_{12}{}^{E}$ as follows[9]:

$$\epsilon_{33}{}^{T}-\epsilon_{33}{}^{S}=\frac{2d_{31}{}^{2}s_{33}{}^{E}+d_{33}{}^{2}(s_{11}{}^{E}+s_{12}{}^{E})-4d_{31}d_{33}s_{13}{}^{E}}{(s_{11}{}^{E}+s_{12}{}^{E})s_{33}{}^{E}-2(s_{13}{}^{E})^{2}}. \tag{21}$$

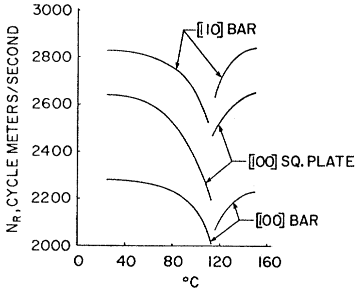

FIG. 2. Temperature variation of fundamental resonance frequency constants for [100] and [110] bars and [100] square plates, 25°C to 150°C.

The elastic compliances s_{11},s_{12}, and s_{44} of the *cubic crystal* were determined by measurements of the fundamental resonance frequencies of [100] bars [Fig. 1(a)], [110] bars [Fig. 1(d)], and [100] square plates [Fig. 1(c)] above the Curie point, by using a maintained bias field of 10 kv/cm. In this case, Eqs. (1) to (3) give a complete set of elastic constants for the cubic crystal. With this bias at 150°C, piezoelectric coupling is so weak that resonance and antiresonance practically coincide.

Data on orthorhombic barium titanate were largely obtained on [100] and [110] bars. Measurements were again made under maintained bias. Elastic compliances have not been calculated from the resonance and antiresonance frequencies, but piezoelectric coupling coefficients were obtained upon assuming a simple transverse expansion [Eq. (7)].

TABLE III. Frequency constants at 150°C.

Test specimen	N_R cycle meters/second
[100] bar	2230
[110] bar	2845
[100] square plate	2650

RESULTS

Average frequency constants of the various bars and plates at 25°C are listed in Table I. The third harmonic of the thickness expansion of the [100] square plates occurred at about 21 Mc/sec, and it was not possible to detect any higher-order harmonics. The value obtained from the third harmonic was therefore used in calculating $c_{33}{}^{D}$ [Eq. (4)]. It was also not possible to detect any higher order harmonics with the thickness shear mode, so the value obtained from the third harmonic was used in calculating $s_{44}{}^{D}$ [Eq. (6)]. The free and clamped permittivities $\epsilon_{11}{}^{T}$ and $\epsilon_{11}{}^{S}$ were measured on plates with thickness along c, but electrodes on edges perpendicular to one of the a axes. In this case, the fundamental resonance frequency was at about 4.8 Mc/sec. The free capacitance was measured at 1 Mc/sec, and the clamped capacitance was determined from measurements in the range 20 to 30 Mc/sec. Free and clamped permittivities $\epsilon_{33}{}^{T}$ and $\epsilon_{33}{}^{S}$ were obtained on face-electroded [100] plates. The free capacitance was measured at about 1 Mc/sec, and the clamped capacitance was determined from measurements in the range 25 to 45 Mc/sec.

Values for all compliances at constant-field and constant-charge density are listed in Table II. Permittivities, piezoelectric constants, and coupling coefficients are also listed in this table. Values compiled by Bechmann[10] for polycrystalline ceramic barium titanate are shown for comparison.

Table III lists average values of measured frequency constants at 150°C, and Table IV shows the complete compliance matrix of the cubic crystal at this temperature.

Figure 2 shows the *temperature dependence* of the fundamental resonance frequencies for [100] and [110] bars and [100] square plates in the range 25 to 150°C. It will be noted that the compliances all become much greater near the Curie point. The temperature dependence of the fundamental resonance frequencies for [100] and [110] bars in the range 25 to −40°C is shown in

TABLE IV. Elastic constants of cubic crystal at 150°C in units of 10^{-12} meter²/newton.

Experimental	Devonshire
$s_{11}=8.33$	9.1
$s_{12}=-2.68$	−3.2
$s_{44}=9.24$	8.2

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[10] R. Bechmann, J. Acoust. Soc. Am. **28**, 347 (1956).

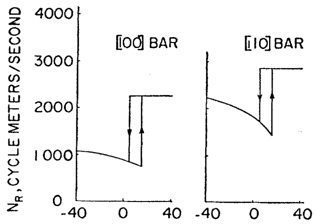

FIG. 3. Temperature variation of fundamental resonance frequency constants for [100] and [110] bars through the tetragonal-orthorhombic transition.

Fig. 3. At the tetragonal-orthorhombic transition the resonance frequencies drop very sharply. Piezoelectric coupling data, obtained from resonance and antiresonance frequencies by assuming a simple transverse expansion in the orthorhombic as well as the tetragonal crystal, are plotted in Fig. 4.

It will be noted that at 25°C the coupling coefficient k_{31} for the [100] bar and k_{31}' for the [110] bar differ (Fig. 4). As we have already seen, the elastic compliance is not single-valued in the (001) plane, i.e., $s_{11}\neq s_{11}'$. The piezoelectric constants are, however, single-valued in the (001) plane, i.e., $d_{31}\equiv d_{31}'$. We may write

$$k_{31}^2=g_{31}d_{31}/s_{11}^E \quad \text{and} \quad k_{31}'^2=g_{31}d_{31}/s_{11}'^E. \tag{22}$$

Therefore,

$$k_{31}'^2=k_{31}^2 s_{11}^E/s_{11}'^E, \tag{23}$$

or

$$k_{31}'=k_{31}N_R'/N_R. \tag{24}$$

A comparison of Figs. 3 and 4 indicates that these data fit the requirement of Eq. (24).

A determination of Poisson's ratio for a [110] bar is rather interesting, since it leads to a negative value. One has

$$s_{12}'=\tfrac{1}{2}s_{11}+\tfrac{1}{2}s_{12}-\tfrac{1}{4}s_{66}=+0.63\times10^{-12}\ \text{m}^2/\text{n}, \tag{25}$$

$$\sigma'^E=-s_{12}'^E/s_{11}'^E=-0.63/5.06=-0.124. \tag{26}$$

A similar negative value is found for the cubic crystal (Table V).

As a check on the elastic constants in the (001) plane, we can use Ekstein's relationship to predict the resonance frequency of a [110] square plate from our values of $s_{11}'^E$ and $s_{12}'^E$. In this case, the predicted value of N_R is 2715 cycle meters/second compared to a measured value of 2690 (Table I). The lack of exact agreement may be attributed to variations in crystal quality, imperfect dimensions of individual plates, and the use of an approximate expression relating s_{11} and s_{12} to the frequency constant of a square plate. It should be pointed out that values of piezoelectric coupling k_{31} for expander bars were quite variable from one specimen to another. Highest values are listed, since these are considered most representative for a true single-domain crystal. Differences in k_{31} were connected with variation in the antiresonance frequency constants, while resonance frequency constants showed little variation between samples. Measuremenrs were made on four or five specimens each of [100] bars, [110] bars, and [100] square plates. Standard deviations from mean values of N_R were, respectively, less than 0.5%, 0.5%, and 0.9%. Only two or three specimens each were used for determination of resonances on [001] bars and side-electroded [100] bars (thickness shear). Variations in N_A and N_A/n respectively were less than 1%. Measurements of c_{33}^D were made on only two plates, and N_A/n was nearly identical for these.

It will be noted that the value for $\epsilon_{33}^T/\epsilon_{33}^S$, calculated from measured values of d_{33}, d_{31}, s_{12}^E, s_{11}^E, s_{33}^E, and s_{13}^E, agrees quite well with the measured value (Table II). Since s_{13}^E was calculated from all the other elastic and piezoelectric constants (except shear), we must consider our value for it the least reliable of the elastic data. The good agreement between the measured and calculated values of $\epsilon_{33}^T/\epsilon_{33}^S$ serves, then, as a confirmation of the value for s_{13}^E.

The elastic constants of single-crystal barium titanate were found to exhibit aging effects after poling similar to, but smaller than, those in the ceramic. Typical data for the crystal are shown in Fig. 5. These data were taken with a signal field of only two millivolts/mm and without a bias field; the crystal was not touched during the aging period. Even very slight mechanical or electric stress can cause rather severe changes in resonance frequencies after removal of the poling field; with a bias field such effects are largely absent. It appears that the aging process is due to stress relief by re-establishment of some 90° twinning.

DISCUSSION OF RESULTS

A comparison of elastic data for the single crystal and the polycrystalline ceramic readily indicates that the anisotropy of the crystal far exceeds that of the poled ceramic. This may be ascribed to the averaging due to random orientation in the ceramic. The poled ceramic has isotropy in the (001) plane, while comparison of Tables II and V shows that the single crystal has large anisotropy in this plane. We can calculate the elastic constants of the unpoled ceramic from the elastic constants of the single crystal. As Devonshire[3] has pointed out, this average can be taken over any one of the matrices s^E, s^D, c^D, or c^E. We chose to average over

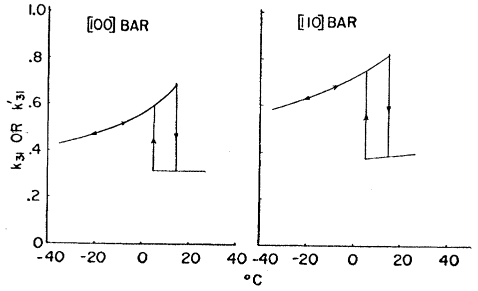

FIG. 4. Temperature variation of the transverse coupling coefficients k_{31} and k_{31}' for [100] and [110] bars through the tetragonal-orthorhombic transition.

s^E, since local piezoelectric fields in the unpoled ceramic should largely cancel. This is borne out by experiments of Moseley,[11] who found that the isotropic compliance of the unpoled ceramic is much closer to $s_{11}{}^E$ and $s_{33}{}^E$ than $s_{11}{}^D$ or $s_{33}{}^D$ of the poled ceramic, and Marutake and Ikeda,[12] who showed that s_{44} for the isotropic ceramic is closer to $s_{44}{}^E$ than $s_{44}{}^D$. The averages are taken as follows; using relationships derived by Voigt[13]:

$$\bar{s}_{11}=(1/5)(2s_{11}+s_{33})+(2/15)(2s_{13}+s_{12})+(1/15)(2s_{44}+s_{66}), \quad (27)$$

$$\bar{s}_{12}=(1/15)(2s_{11}+s_{33})+(4/15)(2s_{13}+s_{12})-(1/30)(2s_{44}+s_{66}), \quad (28)$$

with

$$\bar{s}_{44}\equiv 2(\bar{s}_{11}-\bar{s}_{12}). \quad (29)$$

Resulting calculated values, $s_{11}=7.69$, $s_{12}=-2.82$, and $s_{44}=21.0$, all in 10^{-12} m^2/n, are in fair agreement with Bechmann's[10] s^E for the poled ceramic and hence by references 11 and 12 with experimental s-values for the unpoled ceramic. The fact that the poled ceramic at constant E is not far from elastically isotropic indicates that 90° domain switching plays a relatively small part in the poling process.

The elastic data tabulated in Table II allow some conclusions regarding the bond structure in barium titanate. In both the cubic and tetragonal crystal, the compliance is considerably higher along [100] than [110], indicating that the Ti-O chains are much more compliant than the Ba-O chains. This is confirmed by the high cross-contraction for [100] stress.

In the tetragonal crystal, s_{33} is much higher than s_{11} even at constant D, probably due to weakened bonding between the titanium and the farther removed oxygen. The remarkably high compliances $s_{44}{}^E$ and $s_{44}{}^D$ reflect the loosening of the BaO network in the (100) plane, and perhaps indicate the spontaneous shear in this plane at the transition to the orthorhombic phase.

Table II includes the constants calculated by Devonshire.[3] Devonshire's elastic constants show the type of anisotropy found by our direct experiments, but to a much greater degree. Exact validity of Devonshire's treatment of elastic constants can hardly be expected, however, since his formalism does not take cognizance of the geometric changes at the Curie point, which include three independent atomic parameters.[14] Moreover, the experimental data available to Devonshire were obtained on rather imperfect crystals.

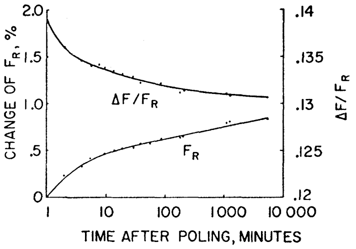

FIG. 5. Aging of the resonance frequency constant and $\Delta F/F_R$ for a prepoled barium titanate crystal disk.

TABLE V. Coefficients for coordinate system rotated 45° around Z axis, in units of 10^{-12} m^2/n.

	Tetragonal 25°C	Cubic 150°C
$s_{11}{}'^E$	5.06	5.13
$s_{11}{}'^D$	4.25	
$s_{12}{}'^E$	+0.63	+0.51
$s_{12}{}'^D$	−0.18	
$s_{66}{}'$	20.8	11.3
$k_{31}{}'$	0.399	

If we regard the piezoelectric effect as an electrostrictive phenomenon of the combined applied signal and spontaneous polarization of the tetragonal crystal, the piezoelectric coefficients g_{33} and g_{31} may be expressed as

$$\partial S_3/\partial P_3=g_{33}=2P_3u_{33}, \quad (30)$$

$$\partial S_1/\partial P_3=g_{31}=2P_3u_{31}, \quad (31)$$

where u_{33} and u_{31} are the electrostrictive coefficients of the cubic crystal with P as independent variable. The coefficients u_{33} and u_{31} can be obtained as the ratios of spontaneous strains of the tetragonal crystal as measured by Kay and Vousden[4] to the square of the spontaneous polarization.[15] We obtain

$$u_{33}=S_3/P_3{}^2=0.0075/(0.26)^2=0.111 \text{ m}^4/\text{coul}^2, \quad (32)$$

$$u_{31}=S_1/P_3{}^2=-0.0030/(0.26)^2=-0.044 \text{ m}^4/\text{coul}^2,$$

$$g_{33}=58\times10^{-3} \text{ volt m/n}, \quad (33)$$

$$g_{31}=-23\times10^{-3} \text{ volt m/n},$$

in excellent agreement with Table II.

The exceptionally high piezoelectric coupling in the orthorhombic state (Fig. 4) is striking and is indeed very surprising in view of the fact that the driving and bias fields are in the [001] direction, while the polar axis is now [011]. This orientation of the polar axis was first indicated by Forsbergh[16] and by Kay and Vousden,[4] and it was recently confirmed by Jona and Pepinsky[17] and by Shirane, Danner, and Pepinsky.[18] Cook, in our laboratory, obtained a further proof by x-ray diffraction studies on ceramic barium titanate. He showed that the longer face diagonal of the orthorhombic phase is oriented preferentially parallel to a high applied electric field.[19]

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[11] D. S. Moseley, J. Acoust. Soc. Am. **27**, 947 (1955).

[12] M. Marutake and T. Ikeda, J. Phys. Soc. Japan **12**, 233 (1957).

[13] W. Voigt, *Lehrbuch der Kristallphysik* (B. G. Teubner, Leipzig, 1910), p. 963.

[14] Shirane, Jona, and Pepinsky, Proc. Inst. Radio Engrs. **43**, 1738 (1955).

[15] W. J. Merz, Phys. Rev. **91**, 513 (1953).

[16] P. W. Forsbergh, Phys. Rev. **76**, 1187 (1949).

[17] F. Jona and R. Pepinsky, Phys. Rev. **105**, 861 (1957).

[18] Shirane, Danner, and Pepinsky, Phys. Rev. **105**, 856 (1957).

[19] W. R. Cook, Jr. (private communication).

At a preliminary state of the present work, the authors[20] tried to explain the remarkably high piezoelectric coupling observed in the orthorhombic state by assuming that the polar axis in the orthorhombic symmetry remained parallel to a cube edge [001]. Another argument was disappearance of the longitudinal resonance on [100] bars at the transition to the orthorhombic state. Later on we found a strong resonance at less than one-half the longitudinal resonance in the tetragonal state (Fig. 3). This astonishing drop in resonance frequency, corresponding to an increase by more than a factor of four in compliance s_{11},[21] is well established by measurement on four specimens, and should be accounted for by any theory of the orthorhombic state.

APPENDIX

The relations between elastic, piezoelectric, and dielectric constants used in this paper follow from the standard piezoelectric equations.[22] By introducing the symmetry of crystal class $4mm=C_{4v}$, we have

$$S_1=s_{11}^E T_1+s_{12}^E T_2+s_{13}^E T_3+d_{31}E_3, \tag{34a}$$

$$S_2=s_{12}^E T_1+s_{11}^E T_2+s_{13}^E T_3+d_{31}E_3, \tag{34b}$$

$$S_3=s_{13}^E T_1+s_{13}^E T_2+s_{33}^E T_3+d_{33}E_3, \tag{34c}$$

$$S_4=s_{44}^E T_4+d_{24}E_2, \tag{34d}$$

$$S_5=s_{44}^E T_5+d_{24}E_1, \tag{34e}$$

$$S_6=s_{66}T_6, \tag{34f}$$

$$D_1=d_{24}T_5+\epsilon_{11}^T E_1, \tag{34g}$$

$$D_2=d_{24}T_4+\epsilon_{11}^T E_2, \tag{34h}$$

$$D_3=d_{31}T_1+d_{31}T_2+d_{33}T_3+\epsilon_{33}^T E_3. \tag{34i}$$

The relations (13), (20), and (21) follow from the set (34) by considering specific combinations of the variables. First, we apply stress T_2 with $T_3=T_1=0$ with electric charge density constant. Equations (34a) and (34i) then become

$$S_1=s_{12}^E T_2+d_{31}E_3,$$
$$0=d_{31}T_2+\epsilon_{33}^T E_3,$$

whence

$$S_1=s_{12}^E T_2-d_{31}^2 T_2/\epsilon_{33}^T,$$

and (13) is obtained in the form

$$S_1/T_2=s_{12}^D=s_{12}^E-d_{31}^2/\epsilon_{33}^T=s_{12}^E-k_{31}^2 s_{11}^E. \tag{13$'$}$$

Next we consider applied stress T_3 with $T_1=T_2=0$, again at constant charge density. In this case, from (34a) and (34i),

$$S_1=s_{13}^E T_3+d_{31}E_3,$$
$$0=d_{33}T_3+\epsilon_{33}^T E_3,$$

whence

$$S_1=s_{13}^E T_3-(d_{31}d_{33}/\epsilon_{33}^T)T_3,$$

and (20) results in the form

$$S_1/T_3=s_{13}^D=s_{13}^E-d_{31}d_{33}/\epsilon_{33}^T=s_{13}^E-g_{33}d_{31}.$$

Finally, we apply a field E_3 to a totally *clamped* crystal, $S_1=S_2=S_3=0$. Equations (34a) and (34b) then require $T_1=T_2$. This reduces the set (34) to

$$0=(s_{11}^E+s_{12}^E)T_1+s_{13}^E T_3+d_{31}E_3, \tag{35a}$$

$$0=2s_{13}^E T_1+s_{33}^E T_3+d_{33}E_3, \tag{35b}$$

$$D_3=2d_{31}T_1+d_{33}T_3+\epsilon_{33}^T E_3. \tag{35c}$$

Also, by definition

$$\epsilon_{33}^S=D_3/E_3. \tag{36}$$

By substituting (36) in (35c), one finds

$$\epsilon_{33}^S=2d_{31}T_1/E_3+d_{33}T_3/E_3+\epsilon_{33}^T. \tag{37}$$

Then by solving the simultaneous equations (35a) and (35b) for T_1/E_3 and T_3/E_3 and substituting into (37), one obtains Eq. (21).

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[20] Berlincourt, Jaffe, and Shiozawa, Bull. Am. Phys. Soc. Ser. II, **1**, 132 (1956).

[21] Referred to cubic axes.

[22] *IRE Standards on Piezoelectric Crystals* (Institute of Radio Engineers, New York, 1949). These Standards were printed in Proc. Inst. Radio Engrs. **37**, 1378 (1949).