

Dependence of the Ratio of Piezoelectric Coefficients on Density and Composition of Barium Titanate Ceramics*

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The ratio of piezoelectric coefficients $-d_{33}/d_{31}$ was found to decrease from about 2.5 for polarized barium titanate ceramic of high porosity to 2.2 for porosity near zero. The ratio increases up to 2.9 for ceramic with 2% porosity containing 12 weight % calcium titanate. For single crystal barium titanate the ratio $-d_{33}/d_{31}$ is 2.5, which checks well with x-ray data for the ratio of thermal strain in the c and a directions. The value for ceramics of lowest porosity does not, therefore, approach that for the single crystal.

THE original x-ray data of Megaw¹ showed no change in the volume of the unit cell as a barium titanate crystal changed abruptly from cubic to tetragonal symmetry at the Curie point. From this Mason² concluded that there should be no volume electrostriction in a barium titanate crystal, and hence that the piezoelectric coefficients should satisfy the relation $d_{33} = -2d_{31}$. This implies that the piezoelectric response to hydrostatic pressure (coefficient d_h) vanishes. He noted, however, that this is not the case with polarized polycrystalline ceramic barium titanate, and that roughly $d_{33} = -2.5d_{31}$. Mason proposed that the inequality in the ceramic was due to the pores which would allow a sidewise contraction of domains without causing a corresponding external contraction, whereas an expansion along the c axis would cause a change in external dimensions.

We have found that in polycrystalline ceramic barium titanate the ratio d_{33}/d_{31} is strongly dependent upon composition. If the above conclusions are correct, on the other hand, one would expect a strong dependence

of this ratio upon density, with the value approaching -2 for density near the theoretical maximum. Our measurements have shown that for a given composition the ratio $-d_{33}/d_{31}$ does indeed decrease as the density increases (see Fig. 1 and Table I). Porosities less than 0.03 were obtained by firing in oxygen. With density increasing from 5.45 to 5.98 g/cc (90.5% to 99.5% of single crystal density), the ratio $-d_{33}/d_{31}$ was found to range from 2.56 to 2.22. Even wider variation in this ratio is, however, available by compositional change, as shown in Fig. 2 and Table II. For a given CaTiO_3 addition the ratio is lower for the purer base material, a barium titanate powder prepared in our laboratories. This may, however, be the result of the lower density obtained with the commercial raw material rather than compositional purity as such.

We have recently measured the piezoelectric coefficients d_{31} and d_h for a barium titanate crystal in the hope of shedding more light on this matter. The crystal selected had very little twinning in relatively large areas as removed from the melt. A small bar 7.0 mm long by 1.5 mm wide by 0.83 mm thick was cut from

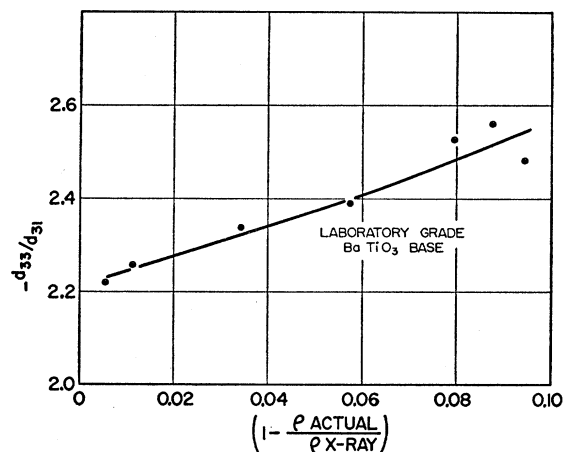


FIG. 1. Ratio of piezoelectric coefficients as function of relative porosity. Porosities less than 0.03 were obtained by firing in oxygen.

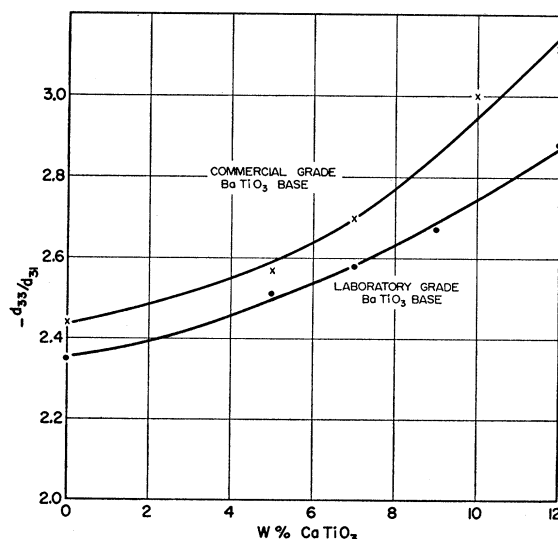


FIG. 2. Ratio of piezoelectric coefficients as function of composition.

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¹ H. D. Megaw, Proc. Roy. Soc. (London) **189**, 261 (1947).

² W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics* (D. Van Nostrand Company, Inc., 1950), pp. 305-306.

TABLE I. Dependence of the ratio d_{33}/d_{31} on density.

Density g/cc	d_{31}^a	d_{33}^a	$-d_{33}/d_{31}$	Porosity $\left(1 - \frac{\rho_{\text{actual}}}{\rho_{\text{x-ray}}}\right)$
5.45	-74.5	184.5	2.48	0.0943
5.49	-78.9	202.4	2.56	0.0875
5.54	-76.4	193.0	2.53	0.0793
5.67	-79.7	190.4	2.39	0.0575
5.81	-79.1	185.2	2.34	0.0344
5.95	-85.0	192.4	2.26	0.0111
5.95	-90.4	203.8	2.26	0.0111
5.98 ₅	-111.2	247.7	2.22	0.0053

^a d in 10^{-12} coulomb/newton.

this crystal with the length along a crystallographic a axis. A poling field of 3 kv/cm was applied as the crystal was cooled through the Curie point in order to prevent "180°" twinning. The piezoelectric coupling coefficient k_{31} was calculated from the resonant and antiresonant frequencies of the fundamental mode. Young's modulus ($1/s_{11}^E$) and the piezoelectric coefficients d_{31} and g_{31} were obtained from the measured frequency constant, "free" dielectric constant, K_{33}^T , and coupling coefficient. Values are listed below:

$$k_{31} = 0.397,$$

$$1/s_{11}^E = 11.3 \times 10^{10} \text{ newtons/m}^2,$$

$$K_{33}^T = 224,$$

$$g_{31} = -26.6 \text{ volt mm/newton},$$

$$d_{31} = -52.6 \text{ micromicrocoulombs/newton}.$$

TABLE II. Dependence of the ratio d_{33}/d_{31} on composition.

% CaTiO ₃	Density g/cc	Density (x-ray) g/cc	d_{31}	d_{33}	$-d_{33}/d_{31}$	Porosity $\left(1 - \frac{\rho_{\text{actual}}}{\rho_{\text{x-ray}}}\right)$
Pure BaTiO ₃ base						
0	5.85	6.017	-97.5	229	2.35	0.028
5	5.70	5.85	-66.6	167	2.51	0.026
7	5.68	5.80	-58.0	150	2.58	0.021
9	5.65	5.74	-52.1	139	2.67	0.016
12	5.55	5.66	-43.4	124.5	2.88	0.019
Commercial BaTiO ₃ base						
0	5.7	6.017	-78.0	190	2.44	0.053
5	5.55	5.85	-58.0	149	2.57	0.054
7	5.47	5.80	-44.3	120	2.70	0.057
10	5.49	5.71	-34.4	103	3.00	0.039
12	5.47	5.66	-30.0	93.6	3.12	0.035

The response to a calibrated hydrostatic pressure was measured, giving $d_h = 26.0$ micromicrocoulombs/newton. The ratio d_{33}/d_{31} for this crystal was thereby found to be -2.50 . Now it is interesting to note that more recent x-ray work of Kay and Vousden^{3,4} gives -2.4 to -2.8 for the ratio of thermal strain in the c and a directions. Thus single crystal data are in accord with the hypothesis that the ferroelectric strains are a function of total polarization. The ratio d_{33}/d_{31} in ceramics of 8% porosity, which is typical of commercial products, is close to that for the single crystal. This agreement is, however, fortuitous; the densest ceramics deviate substantially from single crystals in the ratio d_{33}/d_{31} .

³ H. F. Kay and P. Vousden, *Phil. Mag.* **40**, 1019 (1949).

⁴ H. F. Kay, *Repts. Progr. in Phys.* **18**, 230 (1955).

Effect of Pressure on the Curie Temperature of Polycrystalline Ceramic Barium Titanate*

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The Curie point of polycrystalline barium titanate is found to increase proportionally to the square of an applied planar (two-dimensionally isotropic) compressive stress.

PUBLISHED results on the dependence of the Curie point of single crystal barium titanate on hydrostatic¹ and two-dimensional² compression have stimulated interest in the effects of applied pressure on the Curie point in polycrystalline barium titanate ceramic. Merz¹ found that hydrostatic pressure up to 2.4×10^8 newtons/m² (2500 atmospheres) caused a linear decrease with a slope 5.71×10^{-8} °C/(newton/m²) for the Curie point of a barium titanate crystal. Forsbergh²

found that a two-dimensional pressure in the plane perpendicular to the polar axis of the crystal caused a quadratic increase of the Curie point expressed by 3.0×10^{-15} °C/(newton/m²)². Sawaguchi³ has, however, pointed out that a linear term in the Curie point shift is to be expected theoretically.

The construction of thin spherical shells of barium titanate ceramic led to a means of obtaining substantial two-dimensional compressive stresses. The stress components in an extremely thin spherical shell of radius r and wall thickness t under uniform hydrostatic load P_0

* Work supported by the Office of Naval Research.

¹ W. J. Merz, *Phys. Rev.* **78**, 52 (1950).

² P. W. Forsbergh, Jr., *Phys. Rev.* **93**, 686 (1954).

³ E. Sawaguchi, *Busseiron Kenkyu* **74**, 27 (1954).