

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 <sub>5</sub>	-111.2	247.7	2.22	0.0053

<sup>a</sup>  $d$  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 <sub>3</sub>	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 <sub>3</sub> 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 <sub>3</sub> 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<sup>3,4</sup> 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  $d_{33}/d_{31}$ .

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

<sup>4</sup> 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.

**P**UBLISHED results on the dependence of the Curie point of single crystal barium titanate on hydrostatic<sup>1</sup> and two-dimensional<sup>2</sup> compression have stimulated interest in the effects of applied pressure on the Curie point in polycrystalline barium titanate ceramic. Merz<sup>1</sup> found that hydrostatic pressure up to  $2.4 \times 10^8$  newtons/m<sup>2</sup> (2500 atmospheres) caused a linear decrease with a slope  $5.71 \times 10^{-8}$  °C/(newton/m<sup>2</sup>) for the Curie point of a barium titanate crystal. Forsbergh<sup>2</sup>

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  $3.0 \times 10^{-15}$  °C/(newton/m<sup>2</sup>)<sup>2</sup>. Sawaguchi<sup>3</sup> 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  $P_0$

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<sup>1</sup> W. J. Merz, *Phys. Rev.* **78**, 52 (1950).

<sup>2</sup> P. W. Forsbergh, Jr., *Phys. Rev.* **93**, 686 (1954).

<sup>3</sup> E. Sawaguchi, *Busseiron Kenkyu* **74**, 27 (1954).

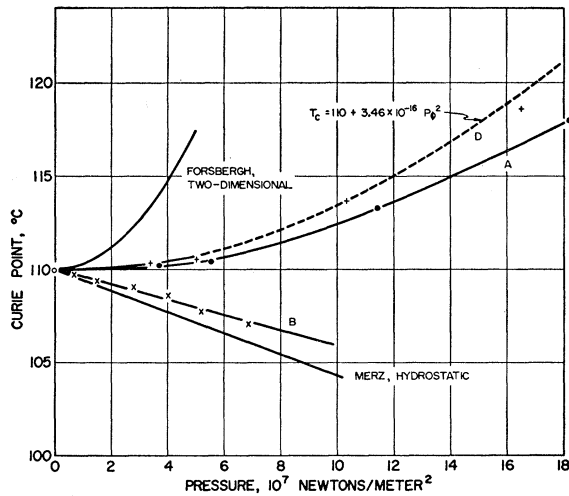


FIG. 1. Curie point dependence on pressure (see text).

on the outside are tangential compressive components  $P_\phi = P_0(r/2t)$  and a radial compression  $P_r$  decreasing from  $P_0$  on the outer to 0 at the inner wall. Average values for  $P_\phi$  and  $P_r$  can readily be calculated for finite wall thickness.<sup>4</sup> The stress tensor for any point in the shell may be regarded as the sum of a hydrostatic stress tensor with three equal orthogonal components  $P_r$  and a two-dimensionally isotropic compression with components  $P_\phi - P_r, P_\phi - P_r, 0$ .

In this investigation, a matched pair of ceramic hemispherical shells, electroded on both surfaces, were joined together with an epoxy cement. The outer diameter and wall thickness of these shells were 4.8 and 0.22 cm, respectively. The electrode connection to the inner spherical surface was brought out at the junction of the hemispheres; the outer surface was not electroded near this connection.

The sphere was placed in an oil-filled pressure vessel, and the desired hydrostatic pressure was applied by a hydraulic pump. An automotive spark plug provided one lead for capacitance measurements, and the metal walls of the pressure vessel provided the other. A thermocouple was attached to the surface of the sphere for accurate temperature determination, and the thermocouple leads were brought out through a gland nut.

The capacitance between the inner and outer spherical surfaces was measured as a function of slowly increasing temperature at several pressure levels. The Curie point, defined as the temperature of minimum inverse dielectric constant, was found to increase approximately quadratically with the applied pressure. In Fig. 1,

<sup>4</sup> A. E. H. Love, *Mathematical Theory of Elasticity* (Cambridge University Press, New York, 1934), Chap. 5, Sec. 98.

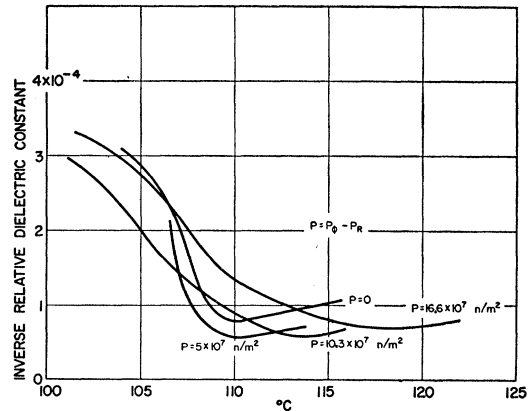


FIG. 2. Inverse dielectric constant vs temperature at several levels of planar stress.

curve A shows this relationship with  $P_\phi$  as abscissa; curve B shows our measurement of Curie point vs hydrostatic pressure for a solid ceramic cylinder. The points near curve D correspond to those on curve A but with pure two-dimensional stress  $(P_\phi - P_r)_{AV}$  as abscissa and shifted upward by a temperature interval equal to the observed shift of the Curie point caused by hydrostatic pressure of magnitude  $(P_r)_{AV}$ . Curve D is a parabola fitted to two points.

The curves of inverse dielectric constant vs temperature (plotted without correction for the influence of the hydrostatic pressure) indicate that the influence of two-dimensional compression on the Curie temperature  $T_c$  in the Curie-Weiss law  $\epsilon = C/(T - T_c)$  is smaller than on the Curie point defined by the maximum of  $\epsilon$  (Fig. 2).

The approximately quadratic increase in the Curie point of polycrystalline ceramic barium titanate with planar compression, as seen in Fig. 1, curve D, is expressed by the relationship:  $T_c = T_0 + 3.46 \times 10^{-16} P^2$ , where  $T_c$  is the Curie point at a stress  $P$  in newtons/m<sup>2</sup> and  $T_0$  the Curie point at zero stress.

The quadratic dependence may be regarded as the product of a domain alignment factor and a linear term according to Sawaguchi's theory. We surmise that Forsbergh's single crystals in his pressure mounting may have shown some 90° domain structure, and that in his case also alignment by stress may have caused a quadratic term in Curie point shift with stress.

We thank Dr. H. G. Baerwald, who suggested the shell as a means of obtaining high two-dimensional stress, for many stimulating discussions; Mr. John Blakesley for preparing the spheres; Mr. Frank Augustine for the pressure equipment; and Mr. Bernard Jaffe, who assisted in some of the measurements.