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INVESTIGATION CONCERNING POLARIZATION IN BARIUM TITANATE CERAMICS

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Investigations Concerning Polarization in Barium Titanate Ceramics

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Synopsis: Considerable information may be obtained concerning polarization in barium titanate ceramics by a careful analysis of hysteresis loops. Mathematically it is shown that both symmetrical and unsymmetrical loops, the latter being characteristic of polarized specimens, can be represented best by a Fourier series. It was found that direct voltage and even harmonic components are present in the unsymmetrical loops. The per-cent second harmonic and the electromechanical coupling coefficient both rise with increasing depolarizing voltage and reach a maximum value at approximately 15,000 volts per cm (centimeter). The measurement of the second harmonic is possible even when the activity is so small that measurement of the coupling coefficient becomes very inaccurate or impossible. The addition of calcium titanate in small percentages markedly raises the coercive force but lowers the spontaneous and remanent polarization in the range from 0 to 80 C (degrees centigrade). However, it does not have marked effect between the latter temperature and the Curie point. It was found from studies of the discharge currents on depolarizing specimens by sudden immersion in hot oil that the polarization observed from the discharge curves is essentially the same as the remanent polarization determined from oscillograms of saturated hysteresis loops.

In RECENT years, many investigations have been made in attempts to elucidate the polarization phenomena of ferroelectrics because of their engineering applications. Of particular interest have been those concerning barium titanate and related compounds having the perovskite structure. The polarization of polydomain ceramic ferroelectrics by the application of an external field consists, in general, of the following processes: 1. the direction of polarization in any crystallite tends to orient in the direction of the applied field, 2. the polarization in the domains increases in magnitude, and 3. the relative volume occupied by different domains changes primarily by growth in the forward direction; sidewise motion of 180 degrees side walls hardly ever occurs.^{1,2} This includes the growth of the induced polarization, much the same linear process as in ordinary dielectrics.

Among the lag and fatigue effects which characterize ferroelectrics is the hysteresis loop. Much knowledge concern-

ing polarization and related properties may be obtained from a careful study of these loops as recorded by means of a cathode-ray oscilloscope.³⁻¹² However, the rate of change of the field for a 60 cycle-per-second hysteresis loop is so rapid that long-time relaxation phenomena which contribute to the polarization are not observed and thus somewhat lower polarization values than the possible maxima are obtained. Recently, by the use of a high-voltage switching and integrating circuit, the relationship between total and remanent polarization to the applied field and applied field duration has been determined at constant temperature for barium titanate ceramics.¹³

For ready reference a representative hysteresis loop for a polycrystalline multidomain ferroelectric is shown in Fig. 1. The variation of polarization P with field strength E is depicted. The spontaneous polarization P_s is obtained by extrapolation of the saturated linear portion of the loop to zero field strength. Note that beyond E , where the linearity commences, the increase in polarization is induced polarization only. Except for the fact that this extrapolated portion does not pass through the origin, it is the same as for ordinary dielectrics. Corresponding to a point E_2 , the total polarization is P_t and the induced polarization $P_i = P_t - P_s$. P_r is the remanent polarization; E_c is the coercive force.

Preparation of Ceramics

In the preparation of ceramics for this investigation, technical grade barium titanate, 97% (per cent); technical grade calcium titanate (96.5%); and chemically pure barium titanate (99.7%) were employed. (All ceramic materials were obtained from the Titanium Alloy Manufacturing Company, Niagara Falls, N. Y.) Disks were prepared for firing by pressing 6 to 10 gm (grams) of sample at 5,000 to 8,000 pounds per square inch in a 1-inch inside diameter mold. No binder was used. The disks were fired in a furnace at 1,350 to 1,370 C from one to two hours. Densities ranged from 5.3 to 5.6 gm per cm³. After machining, the disks were foiled with silver.

Circuit for Recording Hysteresis Loops

For the study of hysteresis loops, in general, previous workers have used a parallel-connected resistance-capacitance voltage divider. However, it was found that a circuit utilizing capacitance voltage dividers only was more suitable for the present purpose. A diagram of this circuit is shown in Fig. 2. Maximum secondary peak voltages of approximately 25 kv per cm could be impressed. Secondary voltages were controlled by means of a Variac. The capacitance voltage divider, consisting of C_1 and C_2 , resulted in a voltage across C_2 directly proportional to the alternating voltage across the ceramic and this voltage was applied to the horizontal plates of the oscilloscope. This voltage is proportional to the electric field E applied to the ceramic. The capacitance of C_2 being much larger than that of C_1 , its effect on the voltage across C_1 may be neglected. Thus, the field intensity across the ceramic is $E = C_2 V_2 / C_1 d$. V_2 is the voltage across C_2 and d is the thickness of the ceramic. C_3 integrates the instantaneous polarizing current i which flows into the ceramic to give a voltage V_3 which is proportional to the polarization P . The capacitance C_4 of the ferroelectric is extremely high compared to that of C_3 . V_3 is then the voltage applied to the vertical plates of the oscilloscope and so the hysteresis loop is observed.

If P is the polarization in coulombs per cm² and a is the area in cm² of an electrode face, then $i = a(dP/dt)$ and $P = (1/a) \int idt$. Since $V_3 = 1/C_3 \int idt$, $P = C_3 V_3 / a$. This last equation enables one to calibrate the axis of ordinates of an oscilloscope.

To check the operation of the circuit the ceramic is replaced by a high-voltage good-quality mica capacitor. Then the resulting trace on the oscilloscope screen should be a straight line with a positive slope when the vertical gain is zero. If the pattern is an ellipse, an undesirable phase shift is present somewhere in the

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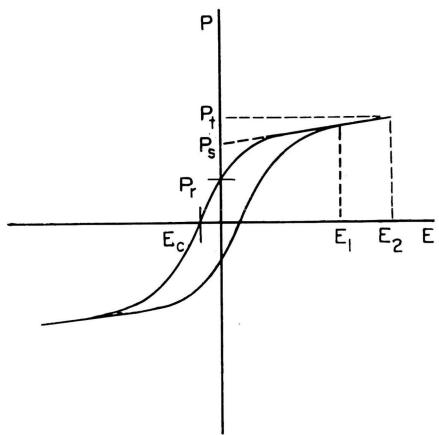


Fig. 1. Representative hysteresis loop for unpolarized ceramic showing variation of polarization P with field strength E . Spontaneous polarization is P_s , remanent polarization P_r , and coercive force E_c .

circuit or in the oscilloscope, and this should be eliminated.

Application of Fourier Series

With varying degrees of success, attempts have been made by a number of investigators to fit various mathematical equations to the magnetization curve of ferromagnetics. Press¹⁴ and Lewis¹⁵ have suggested the use of Fourier series, and in the analysis of the ferroelectric hysteresis loops of barium titanate such a procedure has been used. Accordingly, if

$$x = \left(\frac{E}{E_m} \right) \sin \omega t \quad (1)$$

where E_m is the maximum electric field applied to the specimen and ω is the angular frequency of the sinusoidal variation producing the loop, then

$$y = \frac{P}{P_m} = a_0 + a_1 \cos \omega t + a_2 \cos 2\omega t + \dots + b_1 \sin \omega t + b_2 \sin 2\omega t + \dots \quad (2)$$

where P_m is the maximum polarization and the a 's and b 's are constants for a given hysteresis loop. (It is perhaps well to point out that for barium titanate the dielectric constant is so large that the displacement $D \approx 4\pi P$ in centimeter-gram-second units. D and P can be used interchangeably if meter-kilogram-second units are used.) If the parameter t is eliminated between equations 1 and 2

$$y = (A_0 + A_1 x + A_2 x^2 + A_3 x^3 + \dots) \pm (1 - x^2)^{\frac{1}{2}} (B_0 + B_1 x + B_2 x^2 + B_3 x^3 + \dots) \quad (3)$$

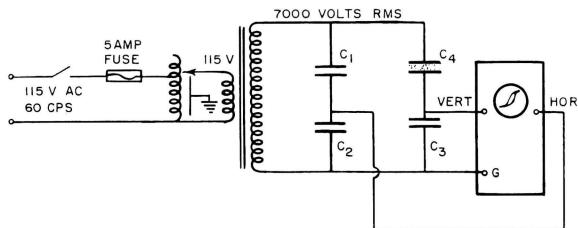


Fig. 2. Circuit for studying hysteresis loop of ferroelectrics. C_1 0.003 μ f, 25 kv; C_2 2.0 μ f, 600 volts; C_3 7.2 μ f, 600 volts; C_4 ferroelectric

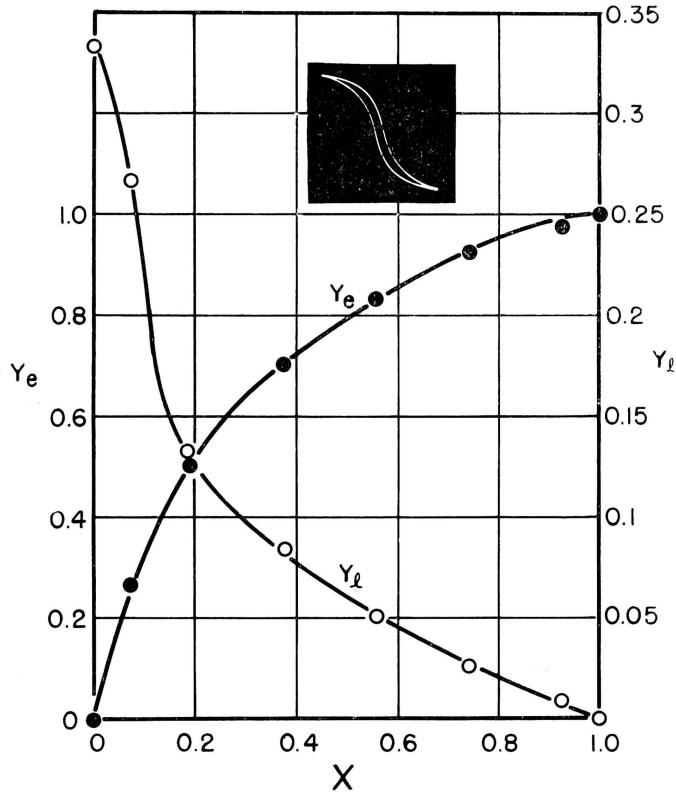


Fig. 3. Curves showing variation of electrization y_e and loss y_l with field strength ratio $x = E/E_m$. Data calculated from measurements on hysteresis loop (insert) for chemically pure ceramic disk of unpolarized BaTiO_3 . $E_m = 11,980$ volts per cm. Calibration cross not shown

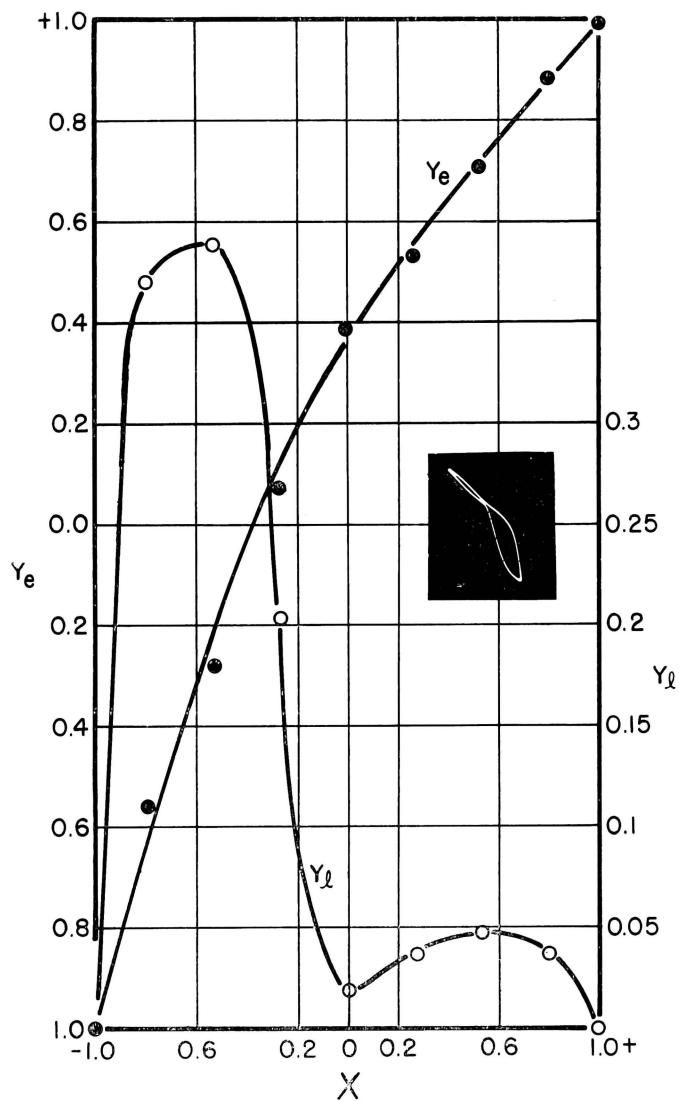


Fig. 4. Curves showing variation of electrization y_e and loss y_l with field strength ratio $x = E/E_m$. Data calculated from measurements on hysteresis loop (insert) for technical grade ceramic disk of polarized BaTiO_3 . $E_m = 9700$ volts per cm. Calibration cross not shown

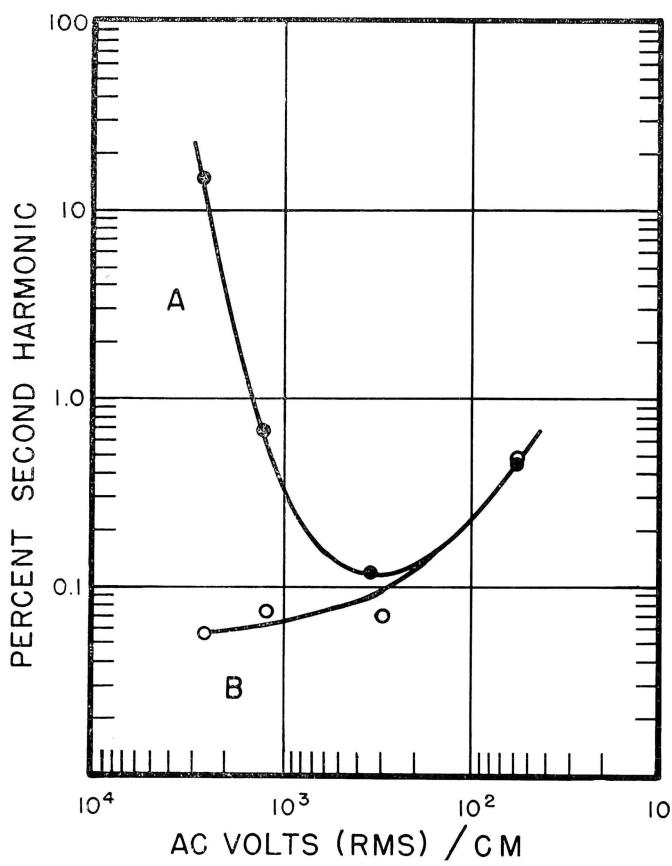


Fig. 5. Percent second harmonic (percentage of the fundamental voltage present) as function of voltage applied to ceramic for:
A—polarized, and
B—unpolarized barium titanate disks

equation 6 and the B 's of equation 7 may be calculated by selecting a number of points on the curves of Fig. 3, and using the number of A 's and B 's equal to the number of points selected. In most cases, however, the experimental curves for y_e and y_l may be fitted adequately with the use of a lesser number of constants by employing special functions such as the hyperbolic tangent or exponential functions.

Polarized specimens of ceramic barium titanate produce unsymmetrical hysteresis loops if the applied alternating voltage is sufficiently high. For an unsymmetrical loop

$$y_a = (A_0 + A_1x + A_2x^2 + \dots) + (1 - x^2)^{\frac{1}{2}} \times (B_0 + B_1x + B_2x^2 + \dots) \quad (8)$$

$$y_b = (A_0 + A_1x + A_2x^2 + \dots) - (1 - x^2)^{\frac{1}{2}} \times (B_0 + B_1x + B_2x^2 + \dots) \quad (9)$$

Then

$$y_e = \frac{1}{2}(y_a + y_b) = (A_0 + A_1x + A_2x^2 + \dots) \quad (10)$$

and

$$y_l = \frac{1}{2}(y_a - y_b) = (1 - x^2)^{\frac{1}{2}} \times (B_0 + B_1x + B_2x^2 + \dots) \quad (11)$$

Electrization and loss curves derived from the hysteresis loop of a polarized disk of barium titanate are shown in the insert of Fig. 4. The upper part of the hysteresis loop is the saturated part, i.e., the direction of polarization and the direction of the applied a-c field are then the same. The larger lower part of the hysteresis loop occurs when the a-c voltage is opposite in direction to that of polarization

where y_e represents the electrization curve (similar to the magnetization curve of ferromagnetism) and y_l represents the loss curve corresponding to the loss as shown by the area of the hysteresis loop.

As an illustration of the procedure to be employed, measurements were first made on the symmetrical hysteresis loop shown in the insert of Fig. 3. Values of y_e and y_l were then calculated and the resulting electrization and loss curves are shown in this figure. The A 's of

where

$$A_0 = a_0 + a_2 + a_4 + a_6 + \dots$$

$$A_1 = b_1 + 3b_3 + 5b_5 + 7b_7 + \dots$$

$$A_2 = -2a_2 - 8a_4 - 18a_6 - 32a_8 - \dots$$

$$A_3 = 4b_3 - 20b_5 - \dots, \text{ etc.}$$

The \pm signs in equation 3 correspond to the upper and lower parts of a given hysteresis loop respectively. It is possible to eliminate the \pm signs entirely by squaring equation 3 to obtain

$$y^2 - 2y(A_0 + A_1x + A_2x^2 + \dots) + (D_0 + D_1x + D_2x^2 + D_3x^3 + \dots) = 0 \quad (4)$$

in which

$$\Sigma D_n x^n = (\Sigma A_m x^m)^2 - (1 - x^2)(\Sigma B_m x^m)^2$$

Equation 4 is the equation of the entire hysteresis loop but for most purposes equation 3 is more useful.

A symmetrical hysteresis loop is one in which the origin of co-ordinates is a center of symmetry and so involves only odd functions. When this fact is utilized, the even A 's and odd B 's are zero so that

$$y = (A_1x + A_3x^3 + A_5x^5 + \dots) \pm (1 - x^2)^{\frac{1}{2}}(B_0 + B_2x^2 + B_4x^4 + \dots) \quad (5)$$

Let y_a represent the upper portion and y_b the lower portion of the symmetrical loop, then

$$(A_1x + A_3x^3 + \dots) = \frac{1}{2}(y_a + y_b) = y_e \quad (6)$$

and

$$(1 - x^2)^{\frac{1}{2}}(B_0 + B_2x^2 + \dots) = \frac{1}{2}(y_a - y_b) = y_l \quad (7)$$

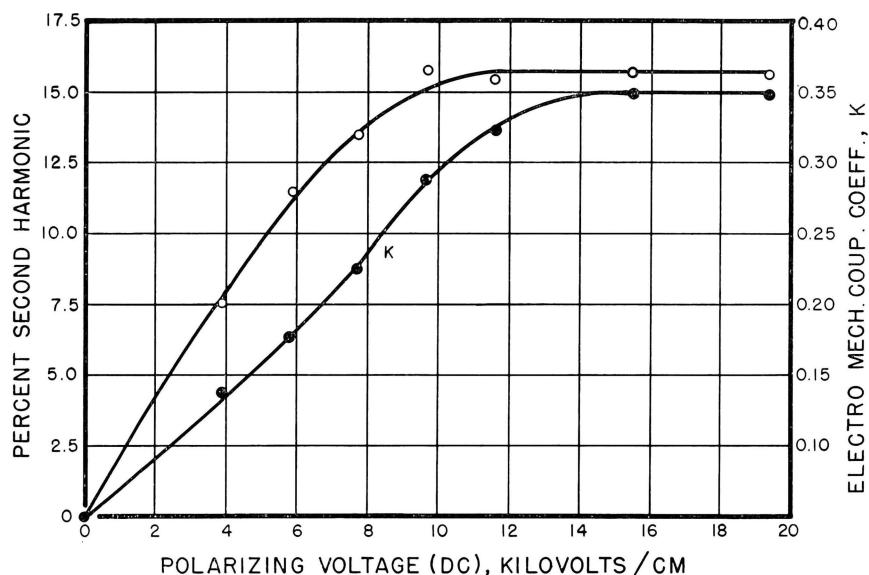


Fig. 6. Rise of percentage second harmonic present and of electromechanical coupling coefficient with increase in polarizing voltage for barium titanate disk

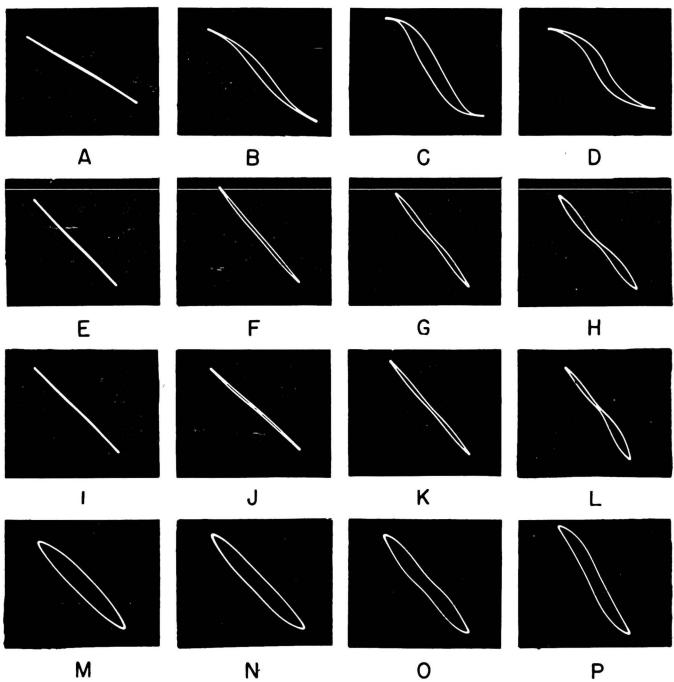


Fig. 7. Variation of form of hysteresis loops with applied alternating voltage:

A-D — unpolarized chemically pure barium titanate
E-H — unpolarized technical grade barium titanate
I-L — polarized technical grade barium titanate
M-P — polarized chemically pure barium titanate. Further data in Tables I and II

from zero. Tests indicated that the d-c component is small.¹⁶

A wave analyzer was connected across capacitor C_3 , Fig. 2, and the harmonics determined for an unpolarized disk and then for one which had been polarized. The polarized specimen responded very similarly to the unpolarized specimen when the alternating voltage was small but, as the alternating voltage was increased, the even harmonics for the polarized specimen became much more prominent. This was particularly true for the second-harmonic voltage. This behavior is indicated by the two curves of Fig. 5, which give the second harmonic as a percentage of the fundamental present. The difference between these curves becomes considerable when the alternating voltage is 2,000 volts rms per cm or more. In work that followed, all of the second-harmonic measurements were made at a fixed voltage of 2,500 volts rms per cm as this magnitude is sufficient to yield a distinct difference between polarized and unpolarized specimens.

To learn whether or not there is any correlation between the electromechanical coupling coefficient and the per-cent second harmonic, an initially unpolarized specimen was polarized at successively increasing direct voltages for one hour at room temperature.

After each period of polarization, the per-cent second harmonic present was

The A 's of equation 10 and the B 's of equation 11 may be determined by selecting a sufficient number of points from Fig. 4. The unsymmetrical shapes of the y_e and y_i curves show that the differential permittivity is larger in the unsaturated direction than it is in the polarized direction.

For theoretical work equation 6 is very useful. Once the constants for any given loop have been determined it is possible to obtain the differential susceptibility, $n_d = \partial P / \partial E$. From equation 3 it follows that

$$\begin{aligned} \left(\frac{\partial P}{\partial E} \right)_{T,C} &= \alpha_0 + \alpha_1 E + \alpha_2 E^2 + \alpha_3 E^3 + \dots \pm \\ &\quad \frac{E}{(E_m - E^2)^{\frac{1}{2}}} (\beta_0 + \beta_1 E + \beta_2 E^2 + \dots) \pm \\ &\quad \left[1 - \left(\frac{E}{E_m} \right)^2 \right]^{\frac{1}{2}} (\beta_1 + 2\beta_2 E + \\ &\quad 3\beta_3 E^2 + \dots) \quad (12) \end{aligned}$$

where

$$\alpha_n = \frac{A_{n+1} P_m}{E_m^{n+1}}; \quad \beta_n = \frac{B_n P_m}{E_m^n}$$

for a given temperature T and composition C .

Corresponding to any point on the hysteresis loop, η_d can be obtained by determining the slope at this point by graphical methods.

Per-Cent Second Harmonic

The unsymmetrical hysteresis loops observed for polarized barium titanate suggest that direct and even harmonic voltage components may be present as a re-

sult of the charge flowing into the ceramic when an alternating voltage is applied. Equations 3 and 5 show that the even A 's and odd B 's are absent when the loop is symmetrical but are present when the loop is unsymmetrical. Since the even A 's and odd B 's are sums of the amplitudes of the direct and even harmonic components, it would seem that some of these components should then be different

Table I. Data Derived from Oscillograms of Hysteresis Loops for Disk of Unpolarized Chemically Pure Ceramic Barium Titanate

Reference Figure	Maximum Field Strength, E_m , Volts per Cm	Coercive Force, E_c , Volts per Cm	Maximum Polarization, P_m , Coulombs per cm^2	Remanent Polarization, P_r , Coulombs per cm^2	Average Dielectric Constant, ϵ_m / ϵ_0	Center Dielectric Constant	End Dielectric Constant
7(A).....	318.....	10.2.....	0.045.....	0.001.....	1,600.....	1,530.....	1,600
7(B).....	714.....	73.6.....	0.170.....	0.021.....	2,700.....	4,330.....	1,450
7(C).....	1,610.....	286.....	1.74.....	0.521.....	12,200.....	23,900.....	1,730
7(D).....	4,200.....	525.....	5.07.....	1.55.....	13,600.....	41,200.....	2,380
3.....	12,000.....	955.....	8.42.....	2.8.....	7,900.....	45,300.....	1,670

Table II. Data Derived from Oscillograms of Hysteresis Loops for Disks of Ceramic Barium Titanate

Disk, Barium Titanate	Reference Figure	Maximum Field Strength, E_m , Volts per Cm	Maximum Polarization, Coulombs per cm^2	Average Dielectric Constant
Technical grade, unpolarized.....	7-e.....	339.....	0.046.....	1,520
	7-f.....	953.....	0.149.....	1,770
	7-g.....	2,940.....	0.638.....	2,450
	7-h.....	6,330.....	2.03.....	3,620
Technical grade, polarized.....	7-i.....	347.....	0.054.....	1,750
	7-j.....	773.....	0.126.....	1,850
	7-k.....	1,930.....	0.394.....	2,320
	7-l.....	3,960.....	1.13.....	3,250
Chemically pure, polarized.....	7-m.....	5,200.....	2.35.....	5,200
	7-n.....	559.....	0.128.....	2,580
	7-o.....	1,770.....	0.544.....	3,480
	7-p.....	4,080.....	2.016.....	5,590
	9,360.....	5.54.....	6,690	
	14,700.....	12.0.....	9,240	

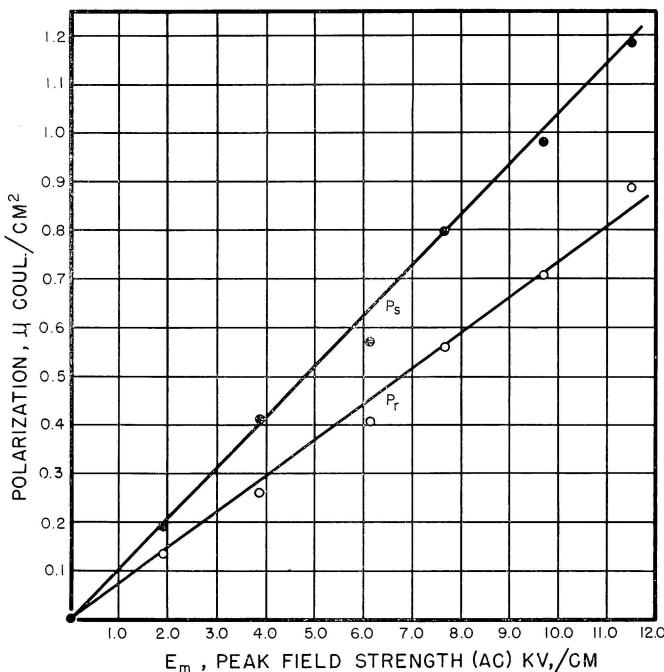


Fig. 8. Linear variation (below saturation) of spontaneous P_s and remanent P_r polarizations with peak field strength E_m for an unpolarized technical grade barium titanate disk. (Data for specimen other than those of Tables I and II)

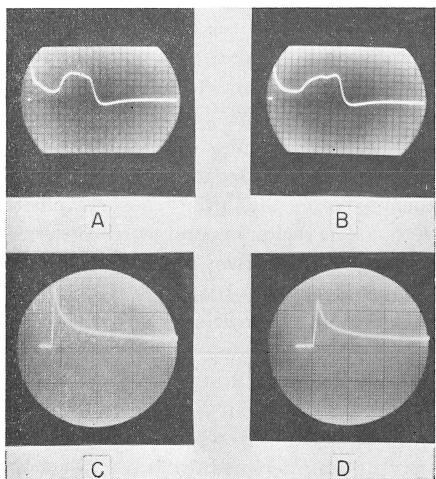


Fig. 10. Representative oscillograms showing depolarization of barium titanate on immersion in oil at 150°C: A, B—0 to 30 seconds; C, D—0 to 3.5 seconds

measured and the electromechanical coupling coefficient calculated from measured values of the resonant and anti-resonant frequencies for the radial mode of vibration. Results are presented in Fig. 6 for the particular experimental conditions described. Both variables rise with increasing polarizing voltage and reach a maximum value at about 15×10^3 volts per cm. Above this voltage no significant improvement in polarization occurs. The per-cent second harmonic rises somewhat faster than the electromechanical coupling coefficient.

Variation of Hysteresis Loops With Applied Voltage

There are a number of factors which determine the form of the hysteresis loop of a ferroelectric, among which are maximum applied a-c field strength, frequency above a certain minimum value, state of polarization if a ferroelectric ceramic is under investigation, chemical purity of the specimen, temperature and, to a certain extent, the total number of domains present. The variation in the form of observed hysteresis loops with applied al-

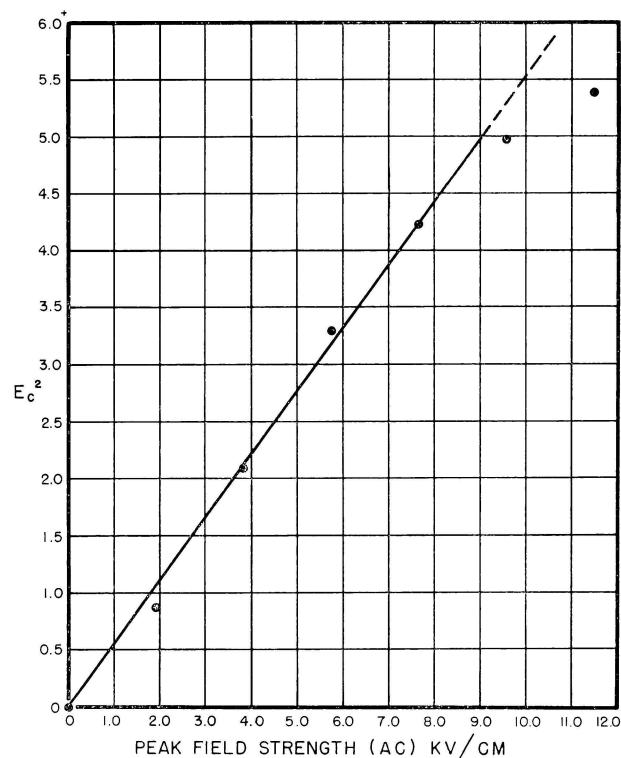


Fig. 9. Linear variation (below saturation) of square of coercive force E_c^2 with peak field strength for unpolarized technical grade barium titanate disk. (Data for specimen other than those of Tables I and II)

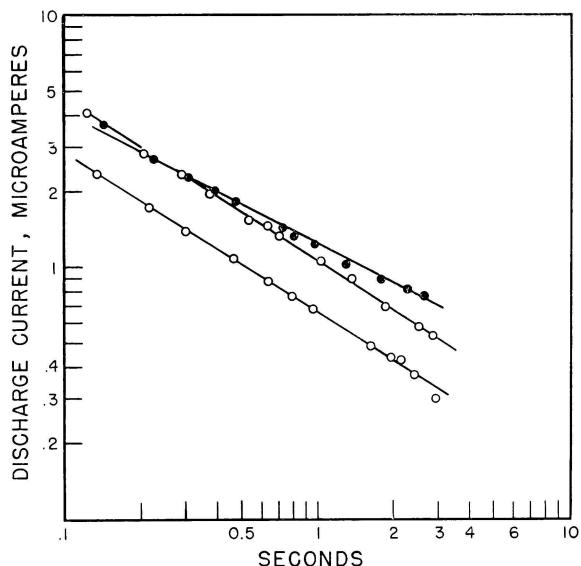


Fig. 11. Logarithmic plot of discharge current versus time after peak current value is reached and before major depolarization of disk occurs

ternating voltage for certain barium titanate ceramics is shown in Fig. 7.

Consider the loops obtained for a disk of unpolarized, chemically pure barium titanate, Fig. 7(A) through (D) and insert of Fig. 3, and those obtained for one of technical grade barium titanate Fig. 7(E) through (H). At low voltages the loop is very nearly a straight line and is similar to that for an ordinary dielectric. The resultant polarization is largely induced and the domain structure is but little affected. As the voltage increases, the center of the loop expands with in-

Table III. Polarization Conditions, Time Corresponding to Peak Current, Constants in Empirical Expression $i = i_0 t^{-m}$, and Initial Discharge Polarization for Ceramic Barium Titanate Disk

Polarization Conditions					
Kv per Cm	Time, Minutes	t_1 , Seconds	i_0 , Amperes	$-m$	P_x , Coulomb per Cm ²
4.....	60.....	0.10.....	0.670.....	0.735.....	0.66.....
8.....	60.....	0.05.....	0.654.....	0.626.....	0.73.....
12.....	60.....	0.08.....	1.176.....	0.626.....	1.91.....
16.....	60.....	0.08.....	1.071.....	0.627.....	1.29.....
16.....	0.083.....	0.10.....	0.343.....	0.639.....	0.21.....
16.....	0.25.....	0.10.....	0.869.....	0.621.....	1.13.....
16.....	0.50.....	0.14.....	0.869.....	0.621.....	1.08.....
16.....	1.0.....	0.12.....	0.869.....	0.821.....	1.11.....
16.....	5.0.....	0.12.....	1.412.....	0.565.....	3.06.....
16.....	15.0.....	0.16.....	1.450.....	0.557.....	3.28.....
16.....	30.0.....	0.16.....	1.450.....	0.557.....	3.37.....
16.....	60.....	0.14.....	1.275.....	0.615.....	2.45.....
16.....	120.0.....	0.14.....	1.209.....	0.553.....	2.17.....

crease in domain orientation. Notice that for the technical grade specimen of barium titanate the saturation effect is not nearly so apparent and the difference between the end and center dielectric constants is small. Also the contraction of the center of the hysteresis loop indicates that both the coercive force and the remanent polarization are relatively small. Data derived from these oscillograms are given in Tables I and II respectively. Note that the center dielectric constant, Table I, increases to very large values while the end dielectric constant changes less markedly. The average dielectric constant P_m/E_m rises to a maximum and then declines after saturation sets in. The spontaneous and remanent polarizations and the square of the coercive force increase nearly linearly with increase in peak field strength over a wide voltage range, as shown in Figs. 8 and 9 respectively. In none of our work on ceramics did the remanent polarization reach the value of approximately 16μ coulombs per cm² measured for saturated single crystals of barium titanate.^{17, 18}

The effect of prior polarization of the barium titanate on the form of the hysteresis loops is shown for a technical-grade specimen in Fig. 7 (I-L); in the insert of Fig. 4; and for a chemically pure high loss specimen in Fig. 7(M) through (P). The noticeable asymmetry in the loop does not appear until the effect of the domain orientation becomes marked which would be in the neighborhood of 3,500 peak volts per cm. For the high-loss specimen the minor axis of the ellipse has expanded considerably over that for low-loss specimens. An ellipse formed at low voltages indicates that the specimen has a relatively high loss.⁴ Variation of maximum polarization and average dielectric constant with field strength are given in Table II for these last two disks.

Several specimens of chemically pure and of technical grade barium titanate

were investigated and the hysteresis loops and results presented here are typical for these respective grades.

High-Temperature Depolarization

Ferroelectrics which have been polarized by a strong d-c field are readily depolarized by heating at temperatures above the Curie point. We have made certain observations concerning this depolarization process. The experimental procedure was to immerse a previously polarized specimen of ceramic barium titanate very suddenly into hot castor oil (150°C) and record the discharge current on an oscillogram. During the first 3 seconds after immersion there is a sudden and rapid loss of charge which declines nearly to zero and thereafter the current again rises and declines, the second process being much slower and taking 10 or more seconds; see Fig. 10. In some instances the discharge curve dropped below the time axis, as shown in the oscilloscopes of Fig. 10. The second process is due to all or any of a number of factors among which are the slow disorientation of the domain structure of the ceramic,

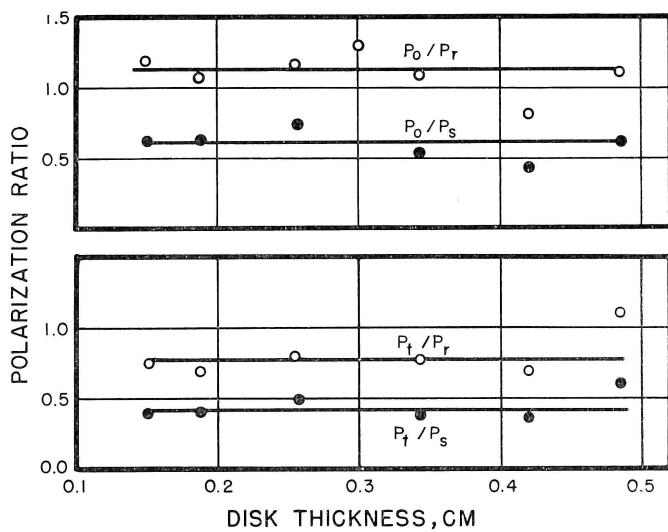
dipole and space charge neutralization, and the electrical double-layer effect. By photographing the discharge process during the first three seconds only, the form of the initial transient can be seen more clearly; see Fig. 10. This transient may be due to the pyroelectric effect in barium titanate. If a logarithmic plot is made of this discharge current versus the time after the peak current value is reached, a straight line results, as shown in Fig. 11. This was found to be true in all cases investigated. The initial current rise, which is negatively limited by the circuit time constants is linear or very nearly so. The decline is represented empirically by the function $i = i_0 t^{-m}$ where i is the discharge current in microamperes, t is the time in seconds, and i_0 and m are constants. The charge P_x released per unit area of disk up to time t_2 is then

$$P_x = \left(\frac{1}{2a} \right) i_0 t_1 + \frac{i_0}{a} \int_{t_1}^{t_2} t^{-m} dt \\ = \left(\frac{1}{2a} \right) i_0 t_1 + \frac{i_0}{a(1-m)} [t_2^{1-m} - t_1^{1-m}] \quad (13)$$

The time at which the current reaches its peak is t_1 , and the area of one face of the disk is a . The charge resulting from the initial rise is determined from the area of the underlying triangle.

In the oscilloscopes of Fig. 10 it is observed that the second discharge commences before the initial transient falls to zero. The region beyond which the overlapping of the two processes becomes serious is perhaps best indicated by the fact that the logarithmic plot is then no longer linear. Thus, where P_x is to be determined for purposes of comparison the upper time limit t_2 has been taken to be that value at which the discharge current has declined to 0.1μ A per cm². Some comparative results are presented

Fig. 12. Polarization ratios versus disk thickness for technical grade of barium titanate ceramics. P_0, P_t = positive and total polarizations from discharge oscilloscopes; P_r, P_s = remanent and spontaneous polarizations from saturated hysteresis loop oscilloscopes



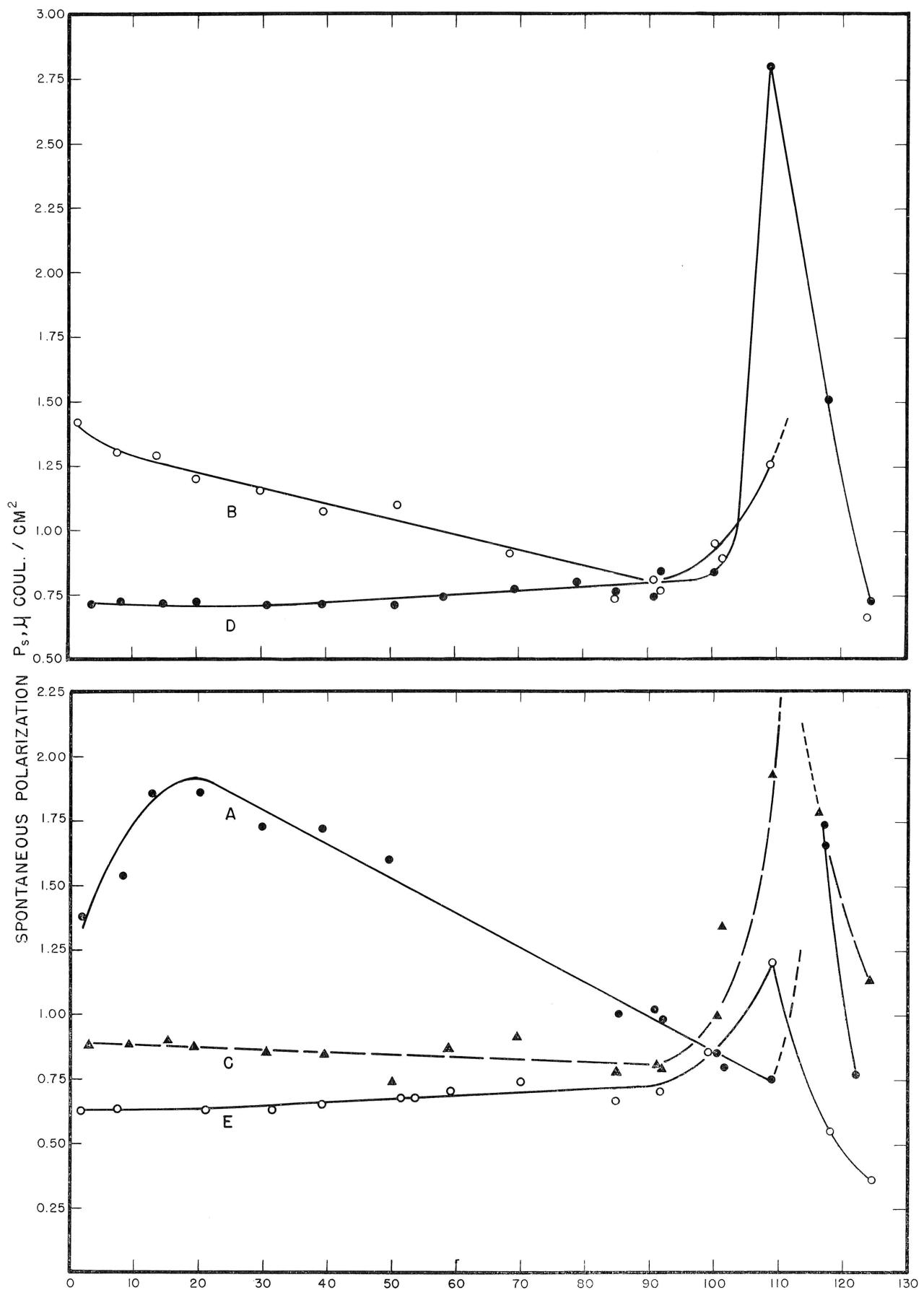


Fig. 13. Variation of spontaneous polarization P_s with temperature for barium titanate ceramics containing: A—No calcium titanate; B—2.5%; C—5.0%; D—7.5%; E—10%

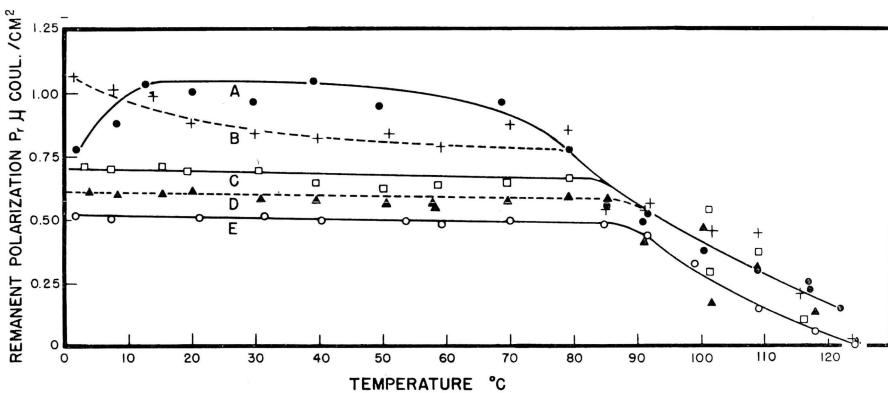


Fig. 14. Variation of remanent polarization with temperature for barium titanate ceramic containing: A—No calcium titanate; B—2.5%; C—5.0%; D—7.5%; E—10%

in Table III for a barium titanate disk polarized under the various conditions given. In each instance the disk was depolarized and an oscillogram taken immediately after polarization. The exponent $-m[d \ln i / d \ln t]$ of equation 13 is very nearly constant. P_x depends on field strength and time of application up to saturation.

It is desirable to correlate, if practicable, the polarization as determined from the area under the discharge curve and one of the degrees of polarization determinable from the saturated hysteresis loop of the same ceramic disk in the unpolarized state. A series of technical grade barium titanate disks was pre-

pared, the thickness of which after machining ranged from 0.15 to 0.5 cm. These were polarized at 16 kv per cm and discharge oscillograms taken 24 hours later. It should be recalled that polarized barium titanate only slowly declines to a more or less metastable condition. Saturated hysteresis loop oscillograms also were obtained for each disk. From the latter were determined the spontaneous polarization P_s and the remanent polarization P_r . From enlarged photographs of the discharge oscillograms, areas under the curves were determined with a planimeter. As previously mentioned, the discharge curve sometimes dropped below the time axis. The polarization calcu-

lated from the area above the time axis will be termed, the positive polarization P_0 , and that positive polarization from which has been subtracted the negative polarization (corresponding to the discharge area below the time axis) will be termed the difference polarization P_t . Respective ratios P_0/P_s , P_t/P_s , P_0/P_r and P_t/P_r were then calculated and the results are plotted in Fig. 12. The curves are straight lines parallel to the axis of abscissas, showing that at least over the range investigated the thickness of the disk did not affect the results. It is observed that the ratio P_0/P_r comes nearest to unity. This seems to indicate that the polarization as determined from the discharge curves is essentially the same as the remanent polarization P_r of the saturated hysteresis loop.

Variation of Spontaneous and Remanent Polarizations, and Coercive Force With Temperature

Hulme was perhaps the first to measure the temperature variation of the spontaneous polarization of a crystal of barium titanate.¹⁹ Later Merz investigated the spontaneous polarization in single crystals along the *c* axis over wide temperature ranges.^{20,21} Discontinuities were found in the polarization-versus-temperature curve wherever a change in crystal class occurs.

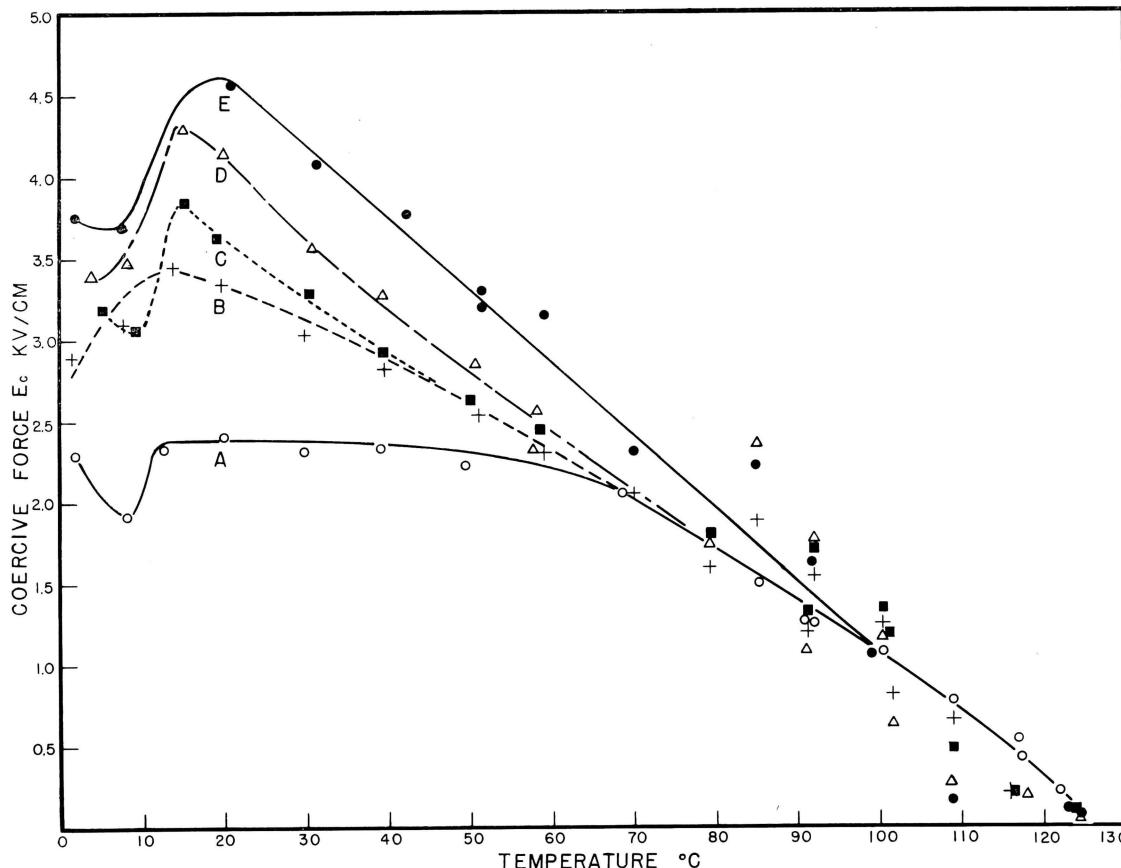


Fig. 15. Variation of coercive force with temperature for barium titanate ceramics containing: A—No calcium titanate; B—2.5%; C—5.0%; D—7.5%; E—10%

This observation is in accordance with the assumption that the spontaneous polarization is parallel to the *c* axis of the crystal when it is tetragonal (approximately from 0 to 120 C), parallel to a face diagonal when the crystal is orthorhombic (approximately from -80 to 0 C), and parallel to the body diagonal when the crystal is trigonal (below -80 C). Merz deduced his data from oscillograms of hysteresis loops. The spontaneous polarization remains nearly constant (8μ coulombs per cm^2) from the -80 C transition temperature down to 4.2 degrees Kelvin (K), the lowest temperature at which measurements were made. The coercive field strength rises sharply from approximately 250 volts per cm at 180 K to over 9,000 volts per cm at 4.2 K.

Apparently no systematic investigation of the variation of polarization with temperature in barium titanate ceramics has been previously reported in the literature. When the spontaneous polarization of a ferroelectric is obtained by extrapolation of the linear saturation branch of the loop to zero field strength, the assumption is made that the induced polarization depends linearly on the field strength and is given by $P_s = (\epsilon - 1) E / 4\pi$. It also assumes that the slope of this branch is determined by the magnitude of the initial dielectric constant which is measured with the use of a weak field and high frequency so that reorientation of domain structure does not occur. However, Rzhanov has shown experimentally that this procedure yields accurate results only outside the region of rapid increase of initial dielectric constant with temperature, i.e., outside the neighborhood of the Curie temperature.¹⁰

The addition of calcium titanate to barium titanate in small percentages results in more uniform electrical properties and greater stability over the important operating range from 0 to 40 C. In general, the magnitudes of the electrical constants are lowered but not excessively lowered.

From saturated hysteresis loop oscillograms of barium titanate ceramic disks,

containing 0, 2.5, 5.0, 7.5 and 10.0 percentages of added calcium titanate, has been determined the remanent polarization P_r , the spontaneous polarization P_s , and the coercive force E_c , over the temperature range from 0 to 125 C. Results are presented in Figs. 13, 14, and 15. Data are for single disks only and thus the results are merely representative. The addition of as little as 2.5% calcium titanate shifts the peak in the remanent and spontaneous polarization curves of ceramic barium titanate to much lower temperatures. Higher percentages serve to linearize and lower the curves, but the effect is less marked as the percentage of added calcium titanate is increased. Marked changes in slope occur between 80 and 100 C.

The coercive force E_c is a measure of the energy necessary to reverse the polar axis of the ferroelectric crystal. The dipoles that result in the spontaneous polarization become reversed in direction. In Fig. 15 are plotted values for coercive force versus temperature for the same group of ceramics as those on which the polarization studies were made, the data having been obtained from the same lot of oscillograms. Peaks occur in these curves at approximately 15 C, i.e., in the neighborhood of the transition temperature from tetragonal to orthorhombic. Thereafter with rise in temperature the coercive force falls rapidly and nearly linearly, dE_c/dt being roughly -40 volts per C except for barium titanate alone, where the change is less marked. Small percentages of added calcium titanate markedly raise the coercive force, showing that the stability of the ceramic has been increased.

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