repulsive force index is but little over the critical value of 5. Undoubtedly the BF_3 molecule becomes "harder" at higher temperatures, as has been noted[7] for NH_3, but one is limited in temperature by the possibilities of increased chemical reactivity and decomposition. We conclude that concentrated B^{10} material may surely be obtained by the thermal diffusion method, but with an over-all efficiency of the plant much too low to make the job attractive.

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[7] W. W. Watson and D. Woernley, Phys. Rev. 63, 181 (1943).

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Dielectric and Piezoelectric Properties of Barium Titanate*

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The dielectric constant and loss of barium titanate and barium-strontium titanate have been measured at biasing field strengths from 0 to 5 megavolts per meter, at temperatures from −50°C to +135°C and at frequencies from 0.1 to 25 megacycles. The measurements *versus* temperature indicate the expected agreement with the Curie-Weiss law at temperatures above the Curie point. Measurements *versus* field strength indicate that the electric field intensity can be expressed as a simple function of the electric displacement, consisting of a linear and a cubic term. At temperatures below the Curie point the results are more complicated, presumably because there are spontaneously polarized domains which give rise to hysteresis and remanence. At field strengths low enough to avoid hysteresis and remanent polarization, no anomalies in the dielectric characteristics *versus* frequency have been observed. When polarized, however, by a momentary application of a strong d.c. field, a resonance spectrum appears in these ceramics. These resonances are attributed to a piezoelectric effect which exists only in the polarized samples. The piezoelectric voltage developed upon squeezing a specimen of polarized barium titanate has been measured directly with a vacuum tube electrometer. Both the longitudinal effect (electric field parallel to mechanical stress) and the transverse effect (field perpendicular to stress) have been observed.

INTRODUCTION

WHILE surveying the properties of a number of titania ceramics, Wainer and Salomon of the Titanium Alloy Manufacturing Company noticed anomalous polarization effects in barium titanate and in solid solutions of barium-strontium titanate.[1] Further studies in the Laboratory for Insulation Research established that these materials constitute a new class of ferroelectric dielectrics.[2,3] $BaTiO_3$ was shown to have a Curie point at about 116°C, coinciding with a lattice transformation from cubic to a structure of lower symmetry, which Megaw and Rooksby[4] identified as tetragonal. The addition of strontium titanate shifted the Curie point and the lattice transformation to lower temperatures. This shifting of the Curie point was followed by Jackson[5] down to −190°C for a composition containing 80 percent strontium titanate. Two additional singularities resembling Curie points have

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[3] A. von Hippel, R. G. Breckenridge, F. G. Chesley, and L. Tisza, Ind. Eng. Chem. 38, 1097 (1946).

[4] H. D. Megaw, Nature, 155, 484 (1945); 157, 20 (1946); Proc. Phys. Soc. Lond. 58, 133 (1946). H. P. Rooksby, Nature 155, 484 (1945).

[5] W. Jackson, and W. Reddish, Nature 156, 717 (1945).

been found for barium titanate[2,3] at about +10°C and −70°C, which become especially pronounced at high field strengths.

The same class of ferroelectrics was studied independently in Russia by Wul.[6] A theoretical paper by Ginsburg[7] was available to the author only after his experimental work had been completed. The experimental results are in essential agreement with Ginsburg's theory.

The ferroelectric character of these materials made it obvious that the ceramics might find useful applications as non-linear dielectrics. Consequently the present study was undertaken to investigate in detail the dielectric constant and loss of barium titanate and barium-strontium titanate *versus* biasing voltage. In the course of the investigation it was found that these materials also have interesting piezoelectric properties.

PREPARATION OF SAMPLES AND MEASURING TECHNIQUES

The dielectric samples were prepared in the form of thin sheets by a method originated by G. Howatt and further developed in this Laboratory.[8] The ceramic powder, obtained from the Titanium Alloy Manufacturing Company, was suspended in a toluene "slip" with a resin binder and, after de-airing, was extruded on a flat baseplate previously coated with a thin film of ethyl cellulose. The extruded sheet, when nearly dry, was stripped from the base and cut in the form of disks $\frac{1}{4}$ inch in diameter, which were fired in a ceramic kiln. The firing temperatures were in the range 1300 to 1500°C for different samples and the time was $\frac{1}{2}$ to 4 hours, the shorter time corresponding to the higher temperature. The thickness of the fired samples ranged between 0.004 and 0.008 inch. Some of the disks were badly warped in firing, but this did not seem to affect their dielectric properties. An electrode of fired-on silver paste about $\frac{1}{8}$ inch in diameter was applied on the top surface and the bottom was covered either with silver paste or with a platinum-foil electrode to which the ceramic fused when it was fired.

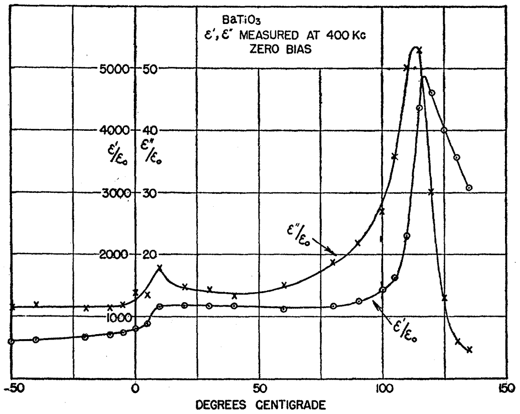

FIG. 1. Dielectric constant and loss factor of $BaTiO_3$ *versus* temperature.

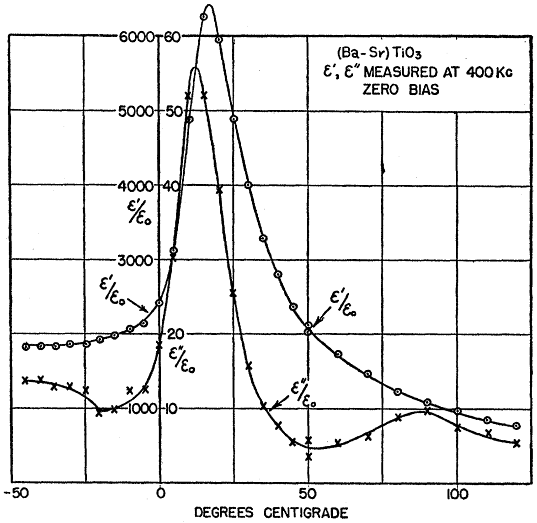

FIG. 2. Dielectric constant and loss factor of $(Ba\text{-}Sr)TiO_3$ *versus* temperature.

The dielectric properties of barium titanate and 75 percent barium/25 percent strontium titanate were derived from impedance measurements of the sample condensers described above. The measurements were made mostly at a frequency of 400 kilocycles per second by means of a radiofrequency bridge, type 916-A (General Radio). In some cases a relatively strong d.c. "biasing" voltage was superimposed on the measuring-frequency voltage in a manner similar to that used by Mueller[9] in measuring nonlinear

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[6] B. M. Wul, and I. M. Goldman, Comptes Rendus U.R.S.S. **46**, 139 (1945); **49**, 177 (1945). B. M. Wul, Nature **156**, 480 (1945); Comptes Rendus U.R.S.S. **51**, 21 (1946); J. Phys. U.S.S.R. **10**, 64 (1946); **10**, 95 (1946); Nature, **157**, 808 (1946). B. M. Wul, and L. F. Vereschagin, Comptes Rendus U.R.S.S. **48**, 634 (1945).

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[8] G. N. Howatt, R. G. Breckenridge, and J. M. Brownlow, J. Am. Ceramic Soc. (to be published).

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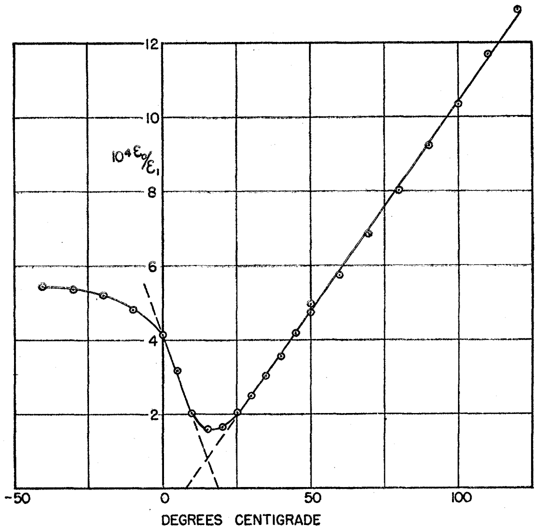

FIG. 3. Reciprocal of dielectric constant of (Ba-Sr)TiO_3 *versus* temperature.

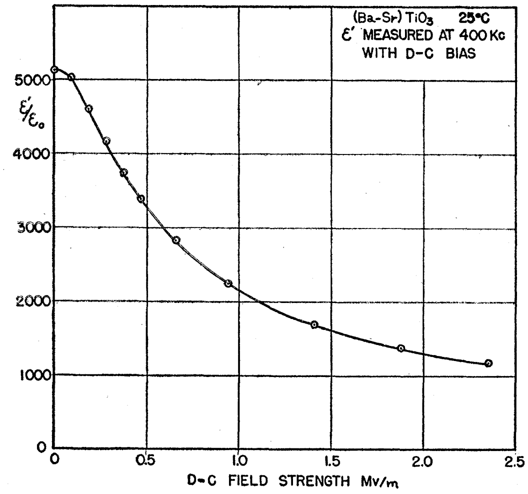

FIG. 4. Dielectric constant of (Ba-Sr)TiO_3 *versus* d.c. field strength.

Rochelle-salt condensers. All of the impedance measurements were made with the sample immersed in an oil bath, which improved the insulation as well as maintaining constant temperature.

EXPERIMENTAL RESULTS

The values of dielectric constant of barium titanate and barium-strontium titanate at low a.c. field strength and in the absence of d.c. bias are shown *versus* temperature in Figs. 1 and 2. In these figures the dielectric constant or permittivity ϵ^* is expressed as a complex quantity in the usual manner in order to account for the dielectric loss.

$$\epsilon^* = \epsilon' - j\epsilon''. \tag{1}$$

The figures show both ϵ' and ϵ'' *versus* temperature.

The temperature at which the dielectric constant of each of these materials has a maximum value has been identified as a Curie point[2, 3, 6, 7, 10] and it has been observed that these materials obey the Curie-Weiss law at temperatures above this point.

$$\epsilon'/\epsilon_0 = \frac{C}{T - T_c}, \tag{2}$$

where:

ϵ_0 = permittivity of free space
C = constant
T = temperature
T_c = Curie temperature (may be a slightly different value from the Curie point mentioned above).

The Curie points indicated by Figs. 1 and 2 are 116°C for barium titanate and 15°C for 75 percent barium/25 percent strontium titanate.

Since Fig. 2 shows ϵ' for barium-strontium titanate in a range of temperature extending considerably above the Curie point, these data can serve as a very good check of the Curie-Weiss law. This is shown in Fig. 3, where $1/\epsilon'$ is plotted *versus* temperature and the experimental points fall on a straight line in accordance with Eq. (2).

At temperatures above the Curie point there is a relatively simple relation between dielectric constant and the d.c. biasing field strength. A typical result is shown in Fig. 4, with the d.c. field strength expressed in megavolts per meter. This curve can be interpreted by postulating a simple equation between the electric field intensity E and the electric displacement D.

$$E = \alpha D + \beta D^3, \tag{3}$$

where α and β are parameters which depend only on temperature. It is noted that Eq. (3) takes no account of losses, which, experiment indicates, are relatively small (<1 percent).

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[10] D. F. Rushman and M. A. Strivens, Trans. Faraday Soc. (to be published).

The permittivity is by definition the slope of the curve of D *vs.* E.

$$\epsilon' = dD/dE. \tag{4}$$

At very small field strengths (zero d.c. bias) the permittivity (initial) is

$$\epsilon_1 = \frac{1}{\alpha} = \frac{\epsilon_0 C}{T - T_c}. \tag{5}$$

By differentiating Eq. (3) and solving the result for D in terms of α, β, and ϵ', and substituting this value of D back in Eq. (3) one obtains

$$\frac{E}{E_0} = \tfrac{1}{4}\left(\frac{\epsilon_1}{\epsilon'} - 1\right)^{\frac{1}{2}}\left(\frac{\epsilon_1}{\epsilon'} + 2\right), \tag{6}$$

where

$$E_0 = 4\left(\frac{\alpha}{3}\right)^{\frac{3}{2}}\beta^{-\frac{1}{2}}. \tag{7}$$

According to Eq. (6), E_0 is simply the field strength required to reduce ϵ' to half its initial value.

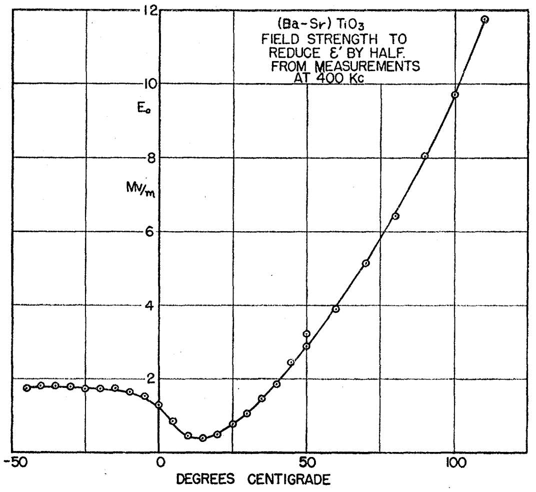

FIG. 5. Critical field strength E_0 of (Ba-Sr)TiO$_3$ *versus* temperature.

TABLE I. Values of $\epsilon_0^3\beta$ in meters^2 volts^{-2} calculated from experimental values of E_0 and ϵ_1 by means of Eq. (8).

Temp. °C	$\epsilon_0^3\beta$	Temp. °C	$\epsilon_0^3\beta$
10	26×10^{-24}	50	7.6×10^{-24}
15	16	60	7.5
20	11	70	7.2
25	9.0	80	7.5
30	8.4	90	7.2
35	7.8	100	7.0
40	7.8	110	6.9
45	7.4		

The experimental results shown in Fig. 4 agree accurately with Eq. (6) if one puts $E_0 = 0.75$ Mv/m, and $\epsilon_1/\epsilon_0 = 5130$.

E_0 is shown *versus* temperature in Fig. 5 for barium-strontium titanate. Even though Eq. (6) is not strictly valid at temperatures below the Curie point, Fig. 5 neverthelss shows values of field strength actually required to reduce ϵ' to half its initial value in this temperature range. Figure 6 gives the corresponding curve for barium titanate. This figure clearly shows the anomalous dielectric response near 10°C at high field strengths previously mentioned.

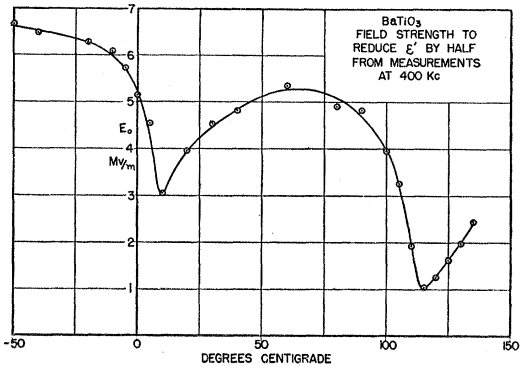

FIG. 6. Critical field strength E_0 of BaTiO$_3$ *versus* temperature.

ϵ_1 and E_0 can be determined experimentally, therefore Eq. (7) can be solved for β.

$$\beta = \frac{16}{27}\frac{\alpha^3}{E_0^2} = \frac{16}{27}\epsilon_1^{-3}E_0^{-2}. \tag{8}$$

Values of $\epsilon_0^3\beta$ have been calculated by means of Eq. (8) and are tabulated for different temperatures in Table I. These results indicate that β is practically constant at temperatures above the Curie point.

The extrapolation of Eq. (3) to temperatures below the Curie point leads as in the ferromagnetic case to the phenomena of hysteresis and spontaneously polarized domains. The curve showing D *vs.* E obtained by extrapolating this equation is given in Fig. 7. Part of this curve is shown with a broken line because it has a negative slope and is therefore unstable. A negative

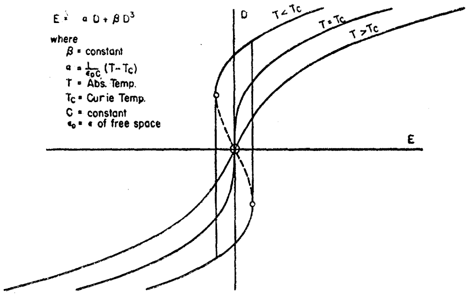

Fig. 7. Theoretical curves for electric displacement *versus* field strength.

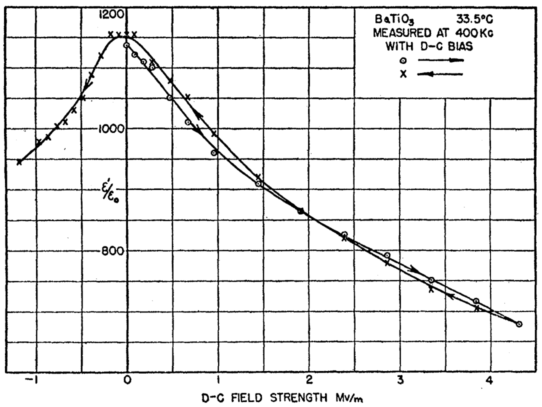

Fig. 8. Dielectric constant of $BaTiO_3$ *versus* d.c. field strength.

slope would correspond to a negative value of static capacitance, which could give rise to exponentially increasing transients. Therefore, as the electric field is shifted, the polarization may be expected to jump suddenly from one branch of the curve to the other along the vertical lines indicated. At zero field strength the electrical displacement cannot be zero but must assume either a positive or negative value determined by the intersections of the curves on the vertical axis.

Although the above interpretation of Fig. 7 is qualitatively correct in that it predicts hysteresis at temperatures below the Curie point, it is inconsistent with the experimental results for two reasons. Firstly, the experimental hysteresis curves do not have the exact shape of Fig. 7, and secondly, the polarization can be zero when the external field is zero. These discrepancies may be resolved by the assumption that the ceramic dielectrics, like other ferroelectric and ferromagnetic materials, are made up of domains, each of which is spontaneously polarized in a direction independent of the others. Figure 7 would then describe the polarization of a single domain.

Hysteresis and remanent polarization have a pronounced effect on the dielectric properties, especially the loss, at temperatures below the Curie point. However, the variation of permittivity *versus* field strength is not always very different from that observed at temperatures above the Curie point. An example is shown in Fig. 8. A detailed description of the non-linear dielectric properties in the range of temperature below the Curie point will be omitted here for the sake of brevity.

In measuring the impedance of the ceramic condensers *versus* frequency, a series of reso-

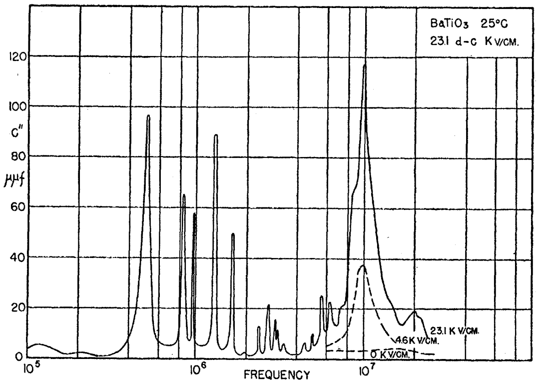

Fig. 9. Loss component of capacitance of $BaTiO_3$ condenser *versus* frequency.

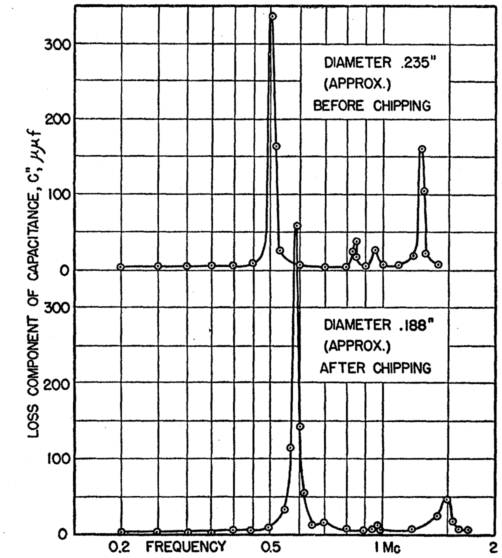

Fig. 10. Loss component of capacitance before and after chipping edge.

nances was found. The impedance is expressed in the form of a complex capacitance.

$$\frac{1}{Z} = j\omega C^* = \omega C'' + j\omega C'. \tag{9}$$

The loss component of capacitance, C'', is shown *versus* frequency in Fig. 9 for a typical sample of barium titanate. The solid line gives C'' when a relatively strong d.c. field is superimposed on the measuring voltage. The lower broken line shows C'' for the unpolarized material, indicating that the resonant losses do not appear in this case. If the ceramic is polarized by applying a strong d.c. field and the field is then turned off, the material retains an appreciable amount of polarization, which is indicated by resonant losses similar to the solid curve in Fig. 9. Resonances of the type shown in this figure tend to disappear at temperatures above the Curie point even when a strong field is maintained.

If the resonances shown in Fig. 9 are to be attributed to a piezoelectric effect, the resonance frequencies must depend on the mechanical dimensions of the ceramic. That this is so was shown by a simple experiment. The resonance frequencies were determined for a disk sample, then pieces of ceramic were broken away from the edge, thereby reducing the effective diameter of the disk. The resonances were shifted to higher frequencies by a constant ratio as a consequence of the reduction in sample diameter. These results are shown in Fig. 10.

A further confirmation of the piezoelectric effect in polarized barium titanate was obtained by squeezing a sample of about $\frac{1}{2}$ inch in diameter and $\frac{1}{8}$ inch in thickness, polarized by momentary application of a d.c. potential of 6000 v. The piezoelectric voltage was measured by means of a vacuum tube electrometer and was found to be several volts for a force of several (not measured) kilograms. Both the longitudinal effect (electric field parallel to mechanical stress) and the transverse effect (field perpendicular to stress) were observed.

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