Published in final edited form as:

J Appl Phys. 1964 May ; 35(5): 1420–1425. doi:10.1063/1.1713643.

Dielectric Breakdown of Single-Crystal Strontium Titanate

Harrison H. Barrett

Raytheon Research Division, Waltham, Massachusetts

Abstract

Measurements of the intrinsic dielectric breakdown strength of single-crystal strontium titanate over a temperature range from -195° to $+100^{\circ}\text{C}$ and under both pulse and dc conditions are described; dc breakdown at $+100^{\circ}\text{C}$ is thermal in origin. At room temperature and at -40°C the breakdown strength is independent of duration of applied field and of sample configuration and hence may properly be termed intrinsic. At -80° and -195°C , both the values of breakdown strength and the scatter of the data depend strongly on sample configuration. The breakdown strength unexpectedly decreases with increasing temperature. Current-voltage curves show an anomalous saturation effect at low temperature. These effects may be qualitatively explained by postulating that the high electrostrictive stress causes the creation of electron trapping centers.

I. INTRODUCTION

AN investigation of the electric strength of nonlinear high-permittivity dielectrics is important since microwave devices which utilize nonlinearity (field dependence of permittivity) must necessarily be subjected to high electric fields. Strontium titanate was a natural choice for this study since its properties have been studied extensively in this laboratory.

The intrinsic dielectric breakdown of alkali halide crystals has been investigated in considerable detail.¹⁻³ A rather simple theoretical model is capable of explaining the temperature dependence and the magnitude of the electric strength of these materials.

Strontium titanate differs from the alkali halides in that its dielectric constant depends strongly on electric field and temperature. Also strontium titanate is strongly electrostrictive at low temperatures. One objective of the present study was to determine if strontium titanate could be described by the same theory that was successful with the alkali halides.

II. SAMPLE SHAPE AND PREPARATION

An important but often ignored feature of high permittivity dielectrics is that the electric field tends to concentrate at the edge of the electrodes.⁴ Therefore any electrode on the surface of a high permittivity solid appears sharp-edged.

The most common method¹ and one adopted in the present study to eliminate spurious breakdown at electrode edges is to use a sample with a hemispherical recess as shown in Fig. 1. The thickness ratio d/t (cf. Fig. 1) depends on the temperature of the test, since both dielectric constant and nonlinearity decrease with increasing temperature. A ratio of 4:1 is sufficient at room temperature, but 12:1 is required at -195°C . With smaller ratios

breakdown occurs through the thick portion at the edge of the plating rather than in the center of the recess. This recessed shape has the additional feature of providing a long path for surface breakdown. The radius of curvature of the recess was normally 0.16 cm.

Boules supplied by National Lead Company were oriented along a [100] axis, sliced with a diamond-loaded slitting saw and cut to the desired shape with an ultrasonic machine tool. The samples were polished by standard techniques. The final polishing agent was 0.3- μ alumina abrasive. They were then cleaned chemically and plated by vacuum evaporation of aluminum.

III. EXPERIMENTAL APPARATUS AND TECHNIQUES

The sample holder was a pressure vessel similar to that described by von Hippel.⁵ Dry nitrogen at about 1000 psi (70 atm) was used to suppress discharges. The vessel was immersed in a constant temperature bath and temperature was measured by means of a gold-cobalt/copper thermocouple.

In order to investigate the effect of rate of application of the field, the high-voltage pulse generator shown in partial schematic in Fig. 2 was constructed. The 0.25- μ F capacitor is charged to the desired voltage from the high-voltage supply and a small portion (~10%) of the charge from this capacitor is then transferred into the 0.025- μ F capacitor by firing the series triggered spark gap. The sample, and a series resistor if desired, is connected across this smaller "reservoir" capacitor. The firing of the gap initiates a preset electronic delay generator or a timer, depending on the pulse width desired. After expiration of the delay a second (shunt) spark gap is fired which terminates the pulse by discharging the 0.025- μ F capacitor and the sample.

Alternatively when long pulses are required the first gap may be bypassed with a switch and the pulse initiated by closing a vacuum relay. This has the advantage of eliminating droop on long pulses if the sample and measuring circuit draw appreciable current. The pulse generator thus has the capability of producing pulses from 10 to 45kV in amplitude, with rise and fall times of 0.5 to 4 μ sec, respectively, and with any desired duration down to a few microseconds.

Pulse measurements are made by inserting an appropriate integrating resistor in series with the sample capacitor. The sample is exposed to a steadily rising voltage ramp until breakdown occurs. The integrating time constant in all tests to date has been a few hundred microseconds.

The sample voltage is measured by means of a capacitive divider and an oscilloscope and camera. Breakdown is observed during the application of a single integrated pulse. This procedure is felt to be preferable to the more common one where a series of square pulses of gradually increasing amplitude is applied. The present technique allows a more precise determination of the breakdown voltage. In addition it minimizes the possibility of irreversible changes occurring in the dielectric before breakdown. For example, it has been found in this study that if a high field is applied to a sample without causing breakdown, it

sometimes happens that the sample may subsequently break down at a field somewhat less than it withstood initially. This fatigue phenomenon has not been investigated in detail.

The dc measurements are made by connecting the sample to the high-voltage power supply. The power supply input voltage is swept up from low values by feeding it from a motor driven variable auto-transformer and the sample is exposed to a linearly rising voltage ramp.

The sample voltage is measured with a resistive voltage divider and feeds one axis of an $X - Y$ recorder. The other recorder axis is used to display the current passing through the samples as measured by an electrometer.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Because of the time required for polishing samples, preliminary measurements were made to determine the effect of polish. The surface condition of the negative electrode is considered most important since electrons could be injected into the bulk material by field emission from sharp discontinuities of this electrode. For this reason the planar surface of the sample is always chosen as the negative electrode since this surface is easier to polish than the hemispherical depression. The results of these experiments are summarized in Table I. It is seen that omitting the fine polish on the planar surface, for pulse measurements at least, greatly increases the scatter in the values of the breakdown field and decreases the mean value somewhat. Applying Fisher's " t " test of significance,⁶ this variation in the means has a probability of 0.57 of being chance. The results for dc measurements are too sparse to be significant, but the trend seems to be the same.

The breakdown tracks observed are of three types, as illustrated in Fig. 3. The desired breakdown is, of course, in the center of the recess since the field there is readily calculable if space-charge effects are neglected. The maximum field between a conducting sphere and plane (a good approximation to our configuration) is, in fact, given by⁷

$$E_{\max} = (V/t) \left[1 + \frac{2}{3}(t/R) + (4/45)(t/R)^2 + \dots \right], \quad (1)$$

where V is the potential difference, R is the radius of the sphere, and t is the separation. The breakdown field may be taken as $E_{\max}$ since the electronic mean free path is much less than t .

The other two types of breakdown shown in Fig. 3 are undesirable. The surface breakdown shown in Fig. 3(c) occurred because of a chip on the edge of the sample. Figure 3(b) shows breakdown at the edge of the plating due to field concentration as discussed above. This occurred at -195°C where SrTiO_3 is quite nonlinear and has a dielectric constant of 2000.

All results obtained are summarized in Table II and Figs. 4 through 9. It is seen that at 100°C dc measurements given a mean breakdown strength of only 92.2 kV/cm while pulse measurements show 779 kV/cm. Even though only four samples have been measured in each case, a thermal breakdown mechanism is clearly indicated under the dc conditions. The pulse value is quite high when compared to lower temperatures (cf. Fig. 9), but this may be because a difficult boule was used.

The mean strength of nine samples at room temperature under pulse conditions is 375 kV/cm while for twelve samples under dc conditions it is 414 kV/cm. According to Fisher's "t" test, this variation has a probability of 0.67 of being chance.

We conclude that there is no significant difference between pulse and dc measurements at room temperature. This seems to preclude thermal effects at room temperature.

Only pulse measurements have been made at -40°C , but there is no reason to suspect that significantly different results would be obtained in dc tests. Furthermore, as the plots of Figs. 4 and 5 indicate, there is no noticeable thickness dependence of the breakdown strength at room temperature or -40°C . Thus at these temperatures the breakdown may properly be termed "intrinsic."

However, the breakdown strength depends markedly on thickness at -80° and -195°C as seen in Figs. 6 to 8. In these cases the results quoted in Table II must be viewed with caution. The standard deviations given are not an accurate measure of the scatter and the mean values depend on the distribution of thickness tested. Also, in addition to the statistical scatter inherent in breakdown experiments, there is a lack of agreement among samples taken from different boules (at -80° and -195°C). There is no definite difference between pulse and dc measurements but the dc values do seem to be slightly higher as they were at room temperature. As seen in Fig. 9, the breakdown strength shows a general decrease with increasing temperature. The accepted theories¹⁻³ of intrinsic breakdown predict the opposite behavior in this temperature range since here electron-phonon interactions are most important in decelerating electrons.

Another important feature to be considered in the low-temperature measurements is their thickness dependence. The existing theories of intrinsic breakdown predict no effect of thickness as long as the sample dimensions are large compared to an electronic mean free path ($\sim 10^{-5}$ cm). The observed behavior suggests that mechanical effects may influence the electrical failure.

Cooper^{8,9} and his co-workers have made a study of the effect of mechanical deformation on electric strength of KCl crystals. They found that annealing the specimens to remove residual strain had the effect of lowering the mean electric strength and reducing scatter by eliminating the higher values. Also, applying external mechanical pressure during breakdown increased the electric strength, and they have presented evidence that mechanical deformation caused by the applied electric field has the same effect. If this latter effect exists in KCl, it should be much more important in SrTiO_3 which is strongly electrostrictive. Cooper *et al.* speculate that plastic deformation affects electric strength through the creation of electron trapping centers in the slip plane. The effect of deformation on scatter of the data is presumably due to variations in the initial mechanical conditions (dislocation density) of the samples.

It is reasonable to expect plastic flow to be greater in an inhomogeneous stress system than in homogeneous one. This supposition provides a reasonable explanation of the observed thickness dependence of electric strength of SrTiO_3 . As the sample is made thicker, the curvature of the recess becomes more important. This increases the shear components of

stress, increasing the amount of plastic flow and, presumably, the density of trapping centers.

It is impossible, on the basis of the data reported here to speculate further about the nature of the traps. However, the only property of the traps that is essential to the arguments presented here is that trap density increase with amount of plastic flow and hence with field inhomogeneity.

To further test this explanation, measurements were made on samples of the same thickness but with varying radius of curvature. As seen in Fig. 10, increasing the radius, i.e., making the sample more nearly plane-parallel, decreases the mean strength and the scatter by eliminating the higher values. This result supports the contention that geometrical stress concentration is an important factor in determining density of trapping centers. [Note the dependence of field inhomogeneity on t/R in Eq. (1).]

Since Cooper *et al.* observed a significant effect with field-induced stresses of less than one psi (0.07 kg/cm^2), it is perhaps surprising that the enormous electrostrictive stress in SrTiO_3 at -195°C does not produce an even greater increase in electric strength. The electrostrictive constants of SrTiO_3 are about a factor of 40 greater at -195°C than at room temperature. The observed increase in electric strength at -195°C is less than a factor of two.

A possible explanation would be that the high electrostrictive stress in the material under high-field conditions at -195°C was such as to cause fracture of the sample which would probably be immediately followed by a destructive electrical discharge through the cracks. After breakdown, the samples were always badly cracked. Direct efforts to observe such an effect were fruitless, but the plausibility of the mechanism may be defended as follows. Low-field measurements of the electrostrictive constant g_{33} by Rupprecht and Winter¹⁰ are pertinent to SrTiO_3 at room temperature. From the temperature dependence predicted by Devonshire's theory¹¹ and confirmed by experimental measurements of g_{31} , the electrostrictive constant g_{33} at -195°C may be estimated. The longitudinal strain can then be calculated for a given applied field. Using this approach, applied fields of 200 kV/cm would be expected to produce a strain of about 45×10^{-3} . The enormous value for this calculated strain suggested that a direct measurement could be made at this temperature and field to confirm the value. A capacitive transducer attached to the sample electrodes was monitored by the apparatus described by Lion¹² and now commercially available.¹³

The results indicate that 200 kV/cm produced a measured strain of 1.5×10^{-3} , i.e., much lower than expected and bordering on the sensitivity of the measuring technique. This low value reflects either a large field dependence of the electrostrictive constant or geometrical clamping, but this is not relevant to the current discussion. It should be emphasized that this strain measurement was quite uncertain because of low sensitivity and the results are only accurate to within about a factor of two.

As may be seen from the stress-strain curve of Fig. 11, this electrostrictive strain is approximately equal to the strain at the yield point of SrTiO_3 at room temperature. No stress-strain curves have been taken at lower temperatures, but the brittle-to-ductile transitions in ionic crystals are usually fairly gradual.^{14,15} In addition, local plastic flow may

occur even if the material does not exhibit macroscopic yield, as evidenced by recent work on germanium.¹⁶

Thus it is reasonable to suppose that plastic flow accounts for the observed thickness dependence and scatter in electric strength at -80°C and that it would cause an even larger effect at -195°C except that fracture occurs first.

Additional indirect evidence for the existence of strain-induced traps is seen in the current–voltage characteristic of Fig. 12. Note that there is about a tenfold decrease in incremental conductivity as the breakdown field is approached. With the samples shown, the d/t ratio was too small so that breakdown occurred at the edge of the plating where the field was grossly inhomogeneous. For samples with an adequate d/t ratio the effect was much less striking. Typically a twofold decrease was observed. In no case was any decrease of conductivity observed at temperatures above -195°C .

V. CONCLUSIONS

The electric strength of single-crystal strontium titanate has been shown to be dependent on sample shape at low temperatures where large electrostrictive strains are developed. It is suggested that strain-induced electron trapping centers increase the electrical strength of the material at -195°C to the point where the electrostrictive stress exceeds the mechanical strength before the applied field exceeds the electrical strength. It has been demonstrated experimentally that the electrostrictive strains are at least of the same order of magnitude of the maximum allowable strain. This proposed mechanism seems to qualitatively account for the observed anomalous features of dielectric breakdown and high-field conductivity in SrTiO_3 .

The suggestion that the ultimate failure is mechanical is not strictly necessary to explain qualitatively the observed geometry and temperature dependence. That behavior can be accounted for simply by the effect of the electrostrictive strain in producing electron trapping centers. However, on the basis of the work of Cooper *et al.*, and the temperature dependence of the electrostrictive constants, a much larger temperature dependence of electric strength would intuitively be expected if fracture did not occur first. The mechanical failure hypothesis is presented here as an alternative explanation which would set an upper limit to the increase in electric strength produced by electrostrictive strain. On the basis of the measurements reported here it is not possible to decide whether this limit is actually reached.

The dielectric breakdown of strontium titanate cannot be directly compared with existing theories because of the unavoidable electrostrictive strain. This effect may be minimized by using a large radius of curvature of the recess and thin samples, but agreement with theory is still not obtained.

Acknowledgments

The author would like to thank B. Wilson for performing much of the experimental work reported here, and P. Nutter, L. Rubin, and J. Welts for many helpful discussions.

References

1. Whitehead, S. Dielectric Breakdown of Solids. Oxford University Press; London: 1953.
2. Stratton R. Progr Dielectrics. 1961; 3:235.
3. O'Dwyer JJ. Phil Mag Suppl. 1958; 7:349.
4. Church HF, Garton CG. Proc Inst Elec Engrs (London). 1953; 100:111.
5. Von Hippel A. Z Physik. 1931; 67:707.1931; 68:309.1932; 75:145.see S. Whitehead (Ref. 1) for an illustration.
6. Fisher, R. Statistical Methods for Research Workers. 13. Hafner; New York: 1958.
7. Attwood, S. Electric and Magnetic Fields. 2. John Wiley & Sons, Inc; New York: 1949. p. 151
8. Cooper R, Wallace A. Proc Phys Soc (London). 1956; 69B:1287.
9. Calderwood J, Cooper R, Wallace A. Proc Inst Elec Engrs (London). 1953; 100:105.
10. Winter W, Rupprecht G. Bull Am Phys Soc. 1962; 7:438.
11. Devonshire AF. Phil Mag. 1949; 40:1040.
12. Lion K. Rev Sci Instr. 1956; 27:222.
13. Decker Corporation, Bala-Cynwyd, Pennsylvania.
14. Hulse CO, Pask JA. J Am Ceram Soc. 1960; 43:373.
15. Murray GT. J Am Ceram Soc. 1960; 43:330.
16. Rindner W, Trampusch RF. J Appl Phys. 1963; 34:758.

Fig. 1.
Sample configuration for dielectric breakdown studies.

Fig. 2.
High-voltage pulse generator, partial schematic.

Fig. 3. Breakdown tracks in SrTiO₃ (a) in recess; (b) at edge of plating; and (c) at surface; (a) is the desirable type.

Fig. 4. Thickness dependence of breakdown field of SrTiO_3 at room temperature (1 mil = 25.4μ).

Fig. 5.
Thickness dependence of breakdown field of SrTiO₃ at -40°C (1 mil=25.4 μ).

Fig. 6.
Thickness dependence of breakdown field of SrTiO_3 at -80°C (1 mil = 25.4μ).

Fig. 7.
Thickness dependence of breakdown field of SrTiO_3 at -195°C (1 mil = $25.4\ \mu$).

Fig. 8.
Thickness dependence of breakdown field of SrTiO₃ at -195°C (1 mil = 25.4 μ).

Fig. 9. Temperature dependence of breakdown strength of SrTiO_3 . Error brackets represent probable error ($0.674 \times \text{standard deviation}$); numbers are the number of samples that were tested. Pulse measurements only. The curves are calculated.

Fig. 10.
Dependence of electric strength of SrTiO_3 on radius of recess (1/32 in. = 0.79 mm).

Fig. 11.
Stress-strain curve for SrTiO_3 at room temperature.

Fig. 12. Current-voltage characteristic of single-crystal SrTiO_3 . The dimensions of the samples are given in inches.

Table I

Effect of polish on electric strength of SrTiO_3 at room temperature.

No. of samples	Polish on planar surface	Polish on recess	Pulse ^a or dc	Breakdown field (kV/cm)			Standard Deviation	
				Min	Mean	Max	(kV/cm)	(%)
9	Linde A ^b	1 μ Diamond	Pulse	315	375	460	42.1	11.2
12	Linde A	1 μ Diamond	dc	315	414	553	73.6	17.8
4	Linde A	Nothing	dc	290	370	470	82.5	22.3
9	600 grit ^c	1 μ Diamond	Pulse	109	302	451	111	42
3	600 grit	Nothing	dc	240	360	440	84	23

^a Pulse measurements were with an integrating time constant of about 400 μsec .

^b Linde A is 0.3- μ grain size alumina.

^c Carborundum.

Table II

Results of dielectric breakdown measurements.

Boule No.	No. of samples	Temp. (°C)	Pulse ^a or dc	Breakdown field (kV/cm)			Standard deviation	
				Min	Mean	Max	(kV/cm)	(%)
ST-7	4	+100	Pulse	648	779	961	107.1	13.8
ST-7	4	+100	dc	73	92.2	131	42.1	22
ST-5+4	9	Room	Pulse	315	375	460	20.1	11.2
ST-4	4	Room	dc	300	430	620	118	27
ST-5	12	Room	dc	315	414	533	73.6	17.8
ST-8	20	-40	Pulse	314	462	646	90	19.5
ST-6	20	-80	Pulse	339	539	941	17.3	32.2
ST-6	10	-80	dc	229	621	1023	242	38.1
ST-6	12	-195	Pulse	255	712	1480	322	45
ST-8	20	-195	Pulse	211	476	807	186	39.2
ST-7	10	-195	dc	312	516	963	187	37.2

^a Integrating time constant about 400 μ sec.^b Electric field in (100) direction.