

TABLE I. Dependence of grain boundary sheet resistivity ρ^* on doping of crystal.

Sample No.	ρ (bulk) $T=300^\circ\text{K}$ (ohm-cm)	Type	Impurity N (atoms/cc)	Type	ρ^* (ohms per square) $T=4.2^\circ\text{K}$
7	1.3	<i>n</i>	1.4×10^{15}	Sb	7800
42	1.6	<i>n</i>	1.1×10^{15}	Sb	5100
6	2.7	<i>n</i>	7×10^{14}	Sb	7500
17	4	<i>n</i>	4.5×10^{14}	Sb	3600
3	5	<i>n</i>	4×10^{14}	Sb	3600
35	27		intrinsic		3600
64	30		intrinsic		5600
29	36		intrinsic		4100
31	4	<i>p</i>	2×10^{14}	Ga	11200
9	1.75	<i>p</i>	3×10^{14}	Ga	8200
11	1.1	<i>p</i>	8×10^{14}	Ga	10200
12	1.1	<i>p</i>	8×10^{14}	Ga	11200
27			10^{16}	Cu	2900
15			10^{16}	Cu	3700
(Tweet ^a)				Au	8000

^a See reference 4.

indicates that the predominant current flow is in the grain boundary. The flattening of the current at low temperatures for the bulk sample is probably due to impurity band conduction. The range of independence from temperature change of grain boundary conduction shown in Fig. 1 is extended to higher temperature in Fig. 2 where rectifying contacts to the *n*-type germanium prevent parallel conduction in the bulk material. In the 2.7 ohm-cm sample the behavior is essentially independent of temperature up to 300°K although it is only shown to 70°K. The 36 ohm-cm sample shows a temperature-independent behavior to 30°K where the poor characteristic of the junctions allows a parallel

leakage path for current through the bulk material. The same temperature independence was found by Tweet in gold-doped bicrystals of the same orientation. The temperature measurements were made in the ohmic range.

The voltage dependence of grain boundary conduction is ohmic in all cases, at least for small applied voltages. In Fig. 3 an *I-V* characteristic is shown which is linear over greater than six decades up to a field of 50 volts/cm. This sample is high-resistivity material with rectifying contacts. In doped samples with ohmic contacts, the bulk material begins to conduct strongly at fields of 5–10 volts/cm due to impact ionization of the impurities. If rectifying contacts are used so that the voltage across the bulk is dropped primarily at the reverse-biased junction, then the voltage difference between the bulk and grain boundary conduction layer introduces a saturating behavior in the *I-V* characteristic at higher voltages. Using values in the linear range, the isolated grain boundary conduction can be characterized by a sheet resistivity ρ^* per square without reference to the thickness of the conducting sheet. In Table I, the behavior of variously doped samples is shown. The values of ρ^* range from 3000–11 000 ohms per square for these samples. This table supports the idea that the grain boundary conductivity is not due to the segregation of impurities—including copper—at the boundary.

Temperature Dependence of the Breakdown Field of Barium Titanate

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The dc breakdown field has been measured for ceramic BaTiO₃ as a function of the ambient temperatures. The breakdown field shows, in general, a temperature dependence of the thermal breakdown type where the breakdown field decreases as the temperature is increased. However, in addition to this general behavior, the breakdown field dips down strongly and shows minima at the critical temperatures of the phase transformations. This seems to indicate a process of polarization breakdown, and is most pronounced near the orthorhombic-tetragonal transition temperatures.

1. INTRODUCTION

THE breakdown field (E_b) of ceramic BaTiO₃ has been measured by Vul, Gol'dman, and Razbush¹; and Sarafanov² with an applied dc field; and by Sarafanov and Skanavi³ with an applied ac field. Vul *et al.* concluded that there is no correlation between E_b and the dielectric constant, while Sarafanov and Skanavi proposed an inverse dependence of E_b on the electrical

conductivity. It is felt that the conclusions of these authors may be based on insufficient experimental data for the following reason: while all the above authors cover a wide temperature range (from about 20°C to 200°C), measurements were made at only five to ten different temperatures. Since BaTiO₃ undergoes a crystallographic phase transformation from the tetragonal phase to the cubic phase at 120°C, the tetragonal phase being ferroelectric and the cubic phase being paraelectric, one might expect that this transformation could influence E_b and because of this, the temperature dependence of E_b might be rather complicated in the temperature region where these authors made their

¹ Vul, Gol'dman, and Razbush, Zhur. Eksptl. i Teoret. Fiz. 20, 465 (1950).

² V. I. Sarafanov, Zhur. Eksptl. i Teoret. Fiz. 27, 590 (1954).

³ V. I. Sarafanov and V. I. Skanavi, Zhur. Eksptl. i Teoret. Fiz. 27, 595 (1954).

measurements. If such a speculation is true (as it was found to be through our experiment), it seems hardly justifiable to draw a conclusion based on data limited to a few temperature values. Therefore, in order to find a more precise relationship between E_b and the temperature, we have measured E_b for ceramic BaTiO₃ with an applied dc field at smaller temperature intervals. The low-temperature range was extended to about -100°C . In extending the temperature, two additional critical temperature regions were covered, namely, the temperatures of the tetragonal-orthorhombic and of the orthorhombic-trigonal phase transformations.

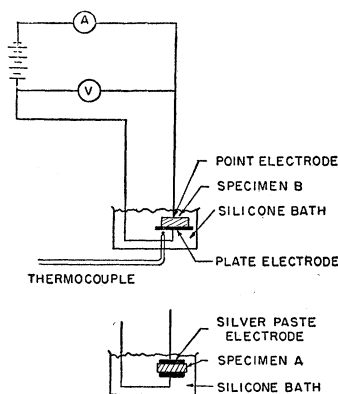
2. EXPERIMENTAL

The specimens of ceramic BaTiO₃ used were in a disk form. Two different materials were used. Specimens Type A were commercial BaTiO₃ for piezoelectric applications and presumably contained a small amount of Ca or Pb. These specimens had a diameter of 0.95 cm, and a thickness of 0.15 cm. The fired-on silver electrode was centered on both faces of the specimen with the silver extending not closer than 1 mm from the edge of the specimen. This electrode configuration was used to prevent breakdown from occurring across the edge of the specimen.

Specimens of Type B were prepared in this laboratory from BaTiO₃ material with impurities less than 0.11%. This high-purity BaTiO₃ was obtained from the thermal decomposition of barium titanyl oxalate⁴ at 500°C . After the material was calcined at 900°C for two hours, it was pressed into disks without using any binder. These disks were covered with BaTiO₃ and fired to 1350°C . The specimens had diameters of 1.5 cm and a thickness of 0.1 cm; and the electrical connection was made by direct contact of the specimens with the specimen holder [Fig. 1(a)].

The specimens were chosen thin enough so that the required voltage would not be so high as to cause partial breakdown, yet of a sufficient thickness that E_b would not depend on the specimen thickness. The effect

FIG. 1. Experimental arrangement (a) (top): for measuring specimens of type B; (b) (bottom): for measuring specimens of type A.



⁴ Barium titanyl oxalate was prepared by W. S. Clabaugh from the procedure reported by Clabaugh, Swiggard, and Gilchrist, J. Research Natl. Bur. Standards **56**, 289 (1956).

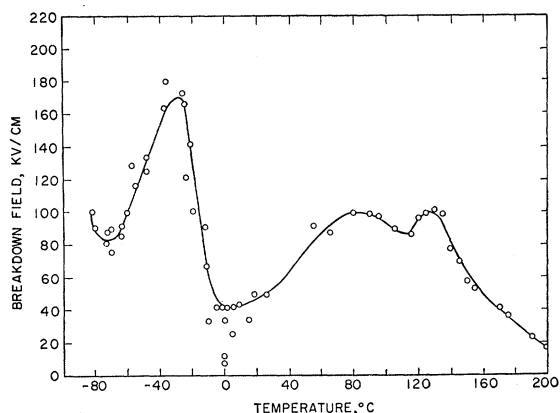


FIG. 2. Temperature dependence of the breakdown field of commercial BaTiO₃.

of the thickness dependence is shown, for example, in biotite mica of thicknesses less than 10^{-3} cm.⁵ The specimens used in this experiment were two orders of magnitude thicker.

The experimental arrangement is shown schematically in Fig. 1(a). The specimen holder consisted of a plate electrode on the bottom, and a nichrome wire contact on the top. For type A specimen the electrode configuration was independent of the specimen holder arrangement. For the type B specimens the electrodes (consisting of the contacts with the specimen holder) were unsymmetrical; however, it was found that the breakdown path was essentially perpendicular to the specimen face from the point electrode, and the cross-sectional area of the breakdown path was less than 0.16 mm^2 , the area of the Nichrome wire. It was felt therefore that the specimen holder configuration would not seriously alter the experimental results.

The ambient temperature for the experiments was obtained by immersing the specimen holder containing the specimen into a silicone oil bath (Dow-Corning 200 fluid). From -70° to about -100°C the liquid became viscous; however, since the values of E_b obtained were still regular, we felt that this viscosity had no unusual effect on the measurements.

After the entire assembly had been cooled and the specimen had reached the desired temperature, a dc field was applied at a rate of about 1 kv/sec. The E_b was obtained during a time interval from 2 to 20 seconds. The effects of the time dependence of E_b were not investigated. When the rate is very slow, in the order of minutes, one would expect some high-field-induced ionic conduction which might decrease E_b .⁶ On the other hand, if the rate of voltage increase is very fast the ferroelectric polarization current, as well as the time lag⁷ of the breakdown voltage, could affect the value of E_b . By using the present rate of voltage

⁵ I. Ryn and H. Kawamura, J. Phys. Soc. Japan **9**, 438 (1954).

⁶ J. Vermer, Physica **22**, 111 (1956).

⁷ Kawamura, Ohkura, and Kikuchi, J. Phys. Soc. Japan **9**, 541 (1954).

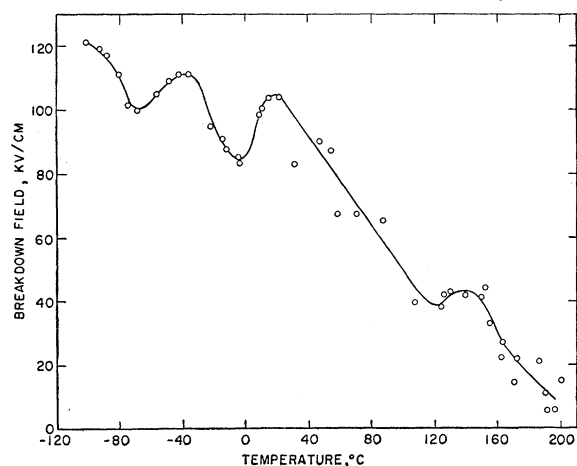


FIG. 3. Temperature dependence of the breakdown field of laboratory specimens of BaTiO_3 from the purified material.

increase, the complications discussed above were presumably avoided.

The value of E_b was taken as the highest voltage observed on the voltmeter when the meter was connected across the specimen. The current was less than 10^{-7} ampere until the breakdown voltage was reached. At the breakdown voltage there was an enormous increase in the current, which exceeded the limitations of the power supply at which time the voltage dropped.

Each Type *A* specimen could be used only once because of the fired-on electrode which covered most of the surface. For Type *B* specimens the point electrode could be moved to a different portion of the specimen and five to seven breakdown measurements could be made at the same or at different temperatures using the same specimen.

3. RESULTS

Values of E_b for Type *A* specimens are shown in Fig. 2. One immediate observation is that E_b has minima near the three transition temperatures, a phenomena that was not reported by the previous authors.¹⁻³

The data in Fig. 2 also indicate that the effect of the depression of E_b near the transition temperature actually extends over a range of temperature.

Figure 3 shows E_b for pure BaTiO_3 specimens. Essentially this has the same features as Fig. 2 with minima occurring at each of the transition temperatures. In addition the figure also shows as a general trend a decrease in E_b as the temperature is increased. Of special interest is the behavior at the orthorhombic-tetragonal transition temperature (at about 0°C). The values for Type *A* specimens are several times lower than those for Type *B* specimens. No explanation can be offered, we can only mention that there was a difference in purity which may have affected E_b .

It can be seen in both Fig. 2 and Fig. 3 that E_b had percentage-wise more scatter near the transition tem-

peratures than it had at other temperatures. This may be expected from the fact that the transition process may not be uniform in different specimens, or in the same specimen.

There are several intrinsic factors which could complicate the measurement of E_b for ceramic BaTiO_3 , such as density, grain size, grain boundaries, and mechanical stresses. With respect to the contribution due to the density, it seems that specimens of high density give high values of E_b while those of low density give low values.⁸ However, it is reasonable to assume that the qualitative features of the temperature dependence of E_b are not changed by the intrinsic factors.

4. CONCLUSIONS

From the results of the experiment the following conclusions can be reached:

(1) Vul *et al.*¹ could not find any correlation between the dielectric constant and E_b . From the results of the present work there is obviously a correlation, namely, at the transition temperatures where the dielectric constant is high, E_b is low and vice versa.

(2) Sarafanov proposed that the breakdown mechanism of BaTiO_3 is a thermal phenomenon due to conduction current, instead of genuine breakdown due solely to the intensity of the high field. This thermal breakdown process could explain qualitatively the lowering of E_b near the 120° transition temperature as there is an indication of a slight increase in conductivity at this point.⁹ However, it should be pointed out that the change in conductivity at this temperature is much less pronounced than the change of E_b . Further verification of Sarafanov's proposal could be obtained from conductivity data at the lower transition temperatures, but unfortunately this is not available at the present time.

Finally, the occurrence of the minima at the temperatures of phase transition may be explained by the instabilities of the domain boundaries at these temperatures. According to the result of Davison¹⁰ on the breakdown of the ferroelectric colemanite, the breakdown passage occurs along the domain boundaries. At the application of the dc field, domains are oriented with the largest gradient along the domain boundaries. Since the domain orientation process is most efficient near the transition, the breakdown field strength would be lowest at the transition temperatures.*

* A. de Bretteville, Jr. (private communication).

⁸ Busch, Flury, and Merz, *Helv. Phys. Acta* **21**, 212 (1948).

⁹ J. W. Davison, *Acta Cryst.* **9**, 9 (1956).

¹⁰ *Note added in proof.*—Since the present manuscript was submitted, two papers have appeared on the same subject: Y. Inuishi and S. Uematsu, *J. Phys. Soc. Japan* **13**, 761 (1958); and Kononova, Kraenopetsev, and Skanavi, *Izvest. Akad. Nauk. Fiz.* **22**, 408 (1958). In both papers the data points are spread over a considerable temperature range. There is not enough detail in either set of data to allow a decision to be made as to the presence or absence of anomalies at the transition temperatures. Inuishi and Uematsu also indicated considerable uncertainty in their single-crystal data, which further obscured the detail.