Electrical Characteristics of High Density, High Purity Titanate Ceramics

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This report is concerned with the electrical behavior of cubic (Ba,Sr)TiO$_3$ ceramics at very high values of the electric field. The work was undertaken to develop a dielectric system to be used in capacitors for the storage and discharge of electrical energy. Objectives for the finished system were to store large amounts of energy per unit volume, to release at least 75% of the energy in $0.2 \times 10^{-6}$ seconds, and to operate over a limited temperature range above 20°C. The work is incomplete, but the results to date show that (Ba,Sr)TiO$_3$ ceramics can store more electrical energy per unit volume than any other known dielectric system.

Since energy storage per unit volume of a dielectric may be represented as:

$$ U = 4.427 \times 10^{-6} \varepsilon' E^2 $$

where $\varepsilon'$ is the dielectric constant, and $E$ is the electric field intensity, in kv/cm,

then, obtaining a material with a high dielectric constant and a high dielectric strength would give maximum energy storage. The problem is to obtain these two parameters simultaneously in the same dielectric.

**COMPOSITION**

The cubic (Ba,Sr)TiO$_3$ system was chosen for study, selecting compositions well above the Curie temperature. Figure 1 shows the dielectric constant (for low voltage alternating fields) as a function of the Ba : Sr ratio in (Ba,Sr)TiO$_3$ solid solutions. It will be noted that a wide range of dielectric constants may be obtained between 30% and 45% (by weight) of SrTiO$_3$ in the solid solution. All compositions to the right of the dielectric constant peak are cubic; those to the left are tetragonal. The two compositions whose properties are reported here are BaTiO$_3$ (60 weight %) -SrTiO$_3$ (40 weight %), and Ba$_2$TiO$_4$ (65 weight %) -SrTiO$_3$ (35 weight %). According to the data shown in Fig. 1, these would have dielectric constant values of 1800 and 3200 respectively.

It was felt that impurities and second phases should be eliminated as much as possible so that the properties studied would be those of the lattice and not of a distribution of flaws. The BaTiO$_3$ and SrTiO$_3$ starting materials were obtained from the Titanium Alloy Manufacturing Division of the National Lead Company, and were that company's chemically pure grade. Of the batches obtained to date, the impurity content has always been less than 0.5%. The major impurities were Group II oxides, SiO$_2$, and Al$_2$O$_3$.

The two titanates were mixed by wet ball milling and then dried, screened and dry pressed. It was found, in air firing to 1300°C, that some local reactions resulted which produced TiO$_2$, Ba$_2$TiO$_4$, and BaTiO$_3$. Accordingly, the ceramics were crushed, pulverized by ball milling, and fired again. In order to obtain flaw-free high density ceramics, it was necessary to control closely the atmosphere-time-temperature relation during the final firing.

With the optimum control of the atmosphere-time-temperature relation, ceramics with striking physical properties were obtained. The pieces were cream-colored, translucent and of very high density. Light could be transmitted through sections up to 8 mm in thickness. The densities ranged from 98.0% to 98.7% of theoretical density as determined from X-ray diffraction patterns. The grain boundaries were sharp and quite narrow. Most ceramic pieces were in the form of disks ranging from 15 to 45 mm in diameter and 1.2 to 8 mm in thickness.

**SAMPLE GEOMETRY**

Upon obtaining ceramics whose physical properties indicated that major flaws had been eliminated, it became necessary to develop a dielectric geometry from which meaningful electrical data could be obtained. The field had to be reduced at the electrode edge so that the maximum electrical stress could be applied to a thin uniform field section. An edge contour which satisfies this requirement may be developed from the field plot for an edge-to-plane configuration in a uniform dielectric medium. This field plot is shown in Fig. 2. The limiting equipotential surface for which the stress is everywhere equal to or less than the stress in the uniform field region is represented by $\psi = 0.5\pi$. This derivation was first made by W. Rogowski, and the surface is usually called the 0.5 Rogowski contour. Electrodes of this shape (or of
lower values to reduce further the edge stress) have been used in the dielectric strength testing of liquids.

The contour selected for use on ceramic samples was the 0.375 Rogowski section shown in Fig. 3. An arbitrary selection of the boundary of the uniform field section was made where the thickness increased by 10%. There was no reason for selecting the edge of the infinite plane as a boundary; at this limit the ceramic thickness increased by 25.4%, which appeared excessive.

The resulting ceramic design is shown in cross-section in Fig. 4. As given above, the effective diameter was measured between the regions where the thicknesses increased by 10%. With an edge thickness at least four times that of the effective central thickness, the problem of flashover (when immersed in oil) was minimized.

A very practical problem was obtaining this contour in ceramics to a nominal precision. It was solved by surface grinding the ceramic disks to obtain uniform thickness and parallel faces, and then grinding the contours ultrasonically. A 500-watt magnetostrictive transducer drove the steel cutting tool. The tolerances on the tool contour were maintained between ±0.01 mm; the ground faces were parallel within 0.02 mm; the thickness was maintained between +0.2 mm. Grinding was done with boron carbide powder (of less than 0.04 mm particle size) suspended in water.

After grinding, a heavy deposit of silver was sputtered over the contoured surface by the technique described by Belser. The ceramics, ready for test, are shown in Fig. 5. A guard electrode, formed on some samples by masking with a circular ring, is displayed on the ceramic on the right.

LOW VOLTAGE TESTS

Low voltage electrical tests were first performed. The dielectric constant and dissipation factor values were nearly constant over the frequency range of 100 cycles per sec to 1 megacycle. Direct current resistivity values were obtained with 100v applied to the samples. Representative data for the two compositions studied are listed in Table 1.

Table 1. Low Voltage Electrical Data on (Ba,Sr)TiO$_3$ Ceramics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Static dielectric constant</th>
<th>Small-signal dielectric constant</th>
<th>Dissipation factor</th>
<th>Resistivity (ohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60/40 Ba : Sr</td>
<td>2500</td>
<td>2120</td>
<td>0.0021</td>
<td>10$^{13}$</td>
</tr>
<tr>
<td>65/35 Ba : Sr</td>
<td>4700</td>
<td>4040</td>
<td>0.0016</td>
<td>10$^{13}$</td>
</tr>
</tbody>
</table>

Original ceramic thickness = 2.5mm or greater
Original ceramic diameter = 17mm or greater
Edge contour = 0.375 Rogowski

Effective thickness = 0.355mm
Effective diameter = 12.7mm
The values shown are conservative; on some samples dissipation factor values of 0.0003 were measured. It should be noted that the small signal dielectric constant values are higher than indicated in Fig. 1. As progressively higher densities were obtained it was found that the dielectric constant increased proportionally. The latest results, at 98.7% of theoretical density, show an increase of approximately 20% over previous data as plotted in Fig. 1.

An unusual trend was noted with the dissipation factor values as the sample density increased. Initially, the dissipation factors were quite low (about 0.0008) but they increased with increasing density. This trend was reversed by regulating the atmosphere carefully during the cooling period following sintering. Optically, it appeared that either excess or deficient oxidation states could be obtained in the high density materials unless great care was exercised in atmosphere control. Undoubtedly the stoichiometric condition is desired, but this is a difficult condition to measure and to obtain throughout a thick specimen. Work is proceeding on this problem.

**HIGH VOLTAGE TESTS**

High voltage testing included dielectric strength measurements and corona testing for voids or unusual conduction mechanisms with both alternating (60 cycles per sec) and static fields. High sensitivity resonant circuit corona test methods were used. It was found that no corona (or any other erratic conduction) occurred with the application of dc fields to breakdown. To date, the dc dielectric strength values, using a rate-of-rise of 100v per second, have ranged from 40 to 180 kv/cm. With the highest density samples the range of values has been 80–180 kv/cm. Higher values than these have been obtained with increased rates of voltage increase. The testing is incomplete; variations within each batch and from batch-to-batch have not yet been isolated so that meaningful distribution curves could be drawn.

To date, the ac corona test appears sensitive to both the microstructure and the macrostructure of the ceramics. At the least, it is a very sensitive test for voids. Corona starting stresses have ranged from 25 to 80 kv/cm.

Some measurements of the dielectric constant and loss have also been made as a function of the applied alternating field. Results obtained to date show a large decrease in dielectric constant and a slight increase in dissipation factor as the field increases. Measurements have not been taken of the low-voltage dielectric constant and loss as determined from a signal superposed on a dc field.

The most important measurements have been those of the stored charge. In this test, the sample was charged by a dc field and then discharged through a ballistic galvanometer. Because of the magnitudes of the potentials and capacitances, the ballistic galvanometer had to be placed in a resistance divider circuit. As this was not a standard technique for ballistic measurements, the resistors were selected with care, and the final assembly was calibrated to ±0.3% using precision air capacitors. In testing samples, the voltage was raised at the rate of 100v per sec to the prescribed level. The sample capacitor was then rapidly disconnected from the supply and discharged through the galvanometer. Two tests were made at each voltage. The voltage was then raised to succeeding test levels until the sample failed.

Figure 5. Contoured ceramics with sputtered silver electrodes

The results, obtained in units of charge, were readily converted into values of dielectric constant. This is a static dielectric constant and must not be confused with the dielectric constant determined with an alternating field. Values of this static dielectric constant are plotted as a function of the field strength in Fig. 6. It will be noted that the dielectric constant, even while decreasing with increasing field, still has high values at the highest fields shown. This is a most important and gratifying result. It demonstrates that the \( (\text{Ba},\text{Sr})\text{TiO}_3 \) system is capable of storing large quantities of electrical energy at high stress.

Finally, the polarization was calculated and plotted as a function of the field in Fig. 7. From this can be drawn the important conclusion that the system under study does not reach saturation polarization at the fields applied. It is obvious that, if saturation does occur, it is at much higher fields. Although the polarization may seem small to one accustomed to the values obtained for the maximum spontaneous polarization for piezoelectric \( \text{BaTiO}_3 \), it is an extremely large number for a non-piezoelectric material. No measurable remanence has been found; the dipoles appear completely dependent on the external field.
DISCHARGE CHARACTERISTICS

It then remained to determine how much of the stored charge was available in very short discharge time intervals. This was determined indirectly using the data in Table 1. Values of the static dielectric constant extrapolated to zero field are listed, and these quantities may be compared with the small signal high frequency dielectric constant values. The static dielectric constants for both compositions are approximately 20% higher than those measured with alternating fields. This means that interfacial polarizations account for only 20% of the stored static charge. Electronic and atomic polarizations intrinsic to the (Ba,Sr)TiO₃ structure account for the bulk of stored energy. All measurements to date give no evidence of relaxation mechanisms (up to 10 megacycles frequency) which would inhibit energy release in very short time intervals. If one pictures the energetic system as a charged particle in a potential well, it appears that the well has smooth sides with no traps. Further, the sides of the well do not rise so steeply as once thought.

Using the values shown in Fig. 6, the energy stored per unit volume may be calculated from Equation (1). For example, at 80 kv/cm the 60/40 Ba : Sr ceramic has an energy storage of 0.48 joules/cm³, while the 65/35 Ba : Sr ceramic stores 0.65 joules/cm³. At 120 kv/cm stress the 60/40 Ba : Sr ceramic stores 0.89 joules/cm³ and the 65/35 Ba : Sr ceramic stores 1.15 joules per cm³. These values are large by comparison with conventional dielectric systems.

A final word must be said concerning sample conditioning. All data reported are for samples in equilibrium with a 23°C ambient at 20-45% relative humidity. Both the dissipation factor values and the interfacial polarization term should be decreased by careful drying. Data are being taken to assess the importance of such conditioning.

It may be concluded that the (Ba,Sr)TiO₃ system has unique properties for energy storage and for low-loss capacitor applications. The importance of purity and control of the sintering operation is established, and may be extended to other ceramic studies. Finally, some interesting applications and new directions of research may be stimulated by this work.

REFERENCES