Properties of Beryllium-Barium Titanate Dielectrics

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Dielectrics having compositions in the system BeO-BaTiO₃-TiO₂ were matured at 1.240° to 1.525° C. Data are given for the compositions, heat-treatments, absorption, and 1,240 to 1,525 C. Data are given for the compositions, heat-treatments, absorption, and shrinkage. At 25° C the dielectric constant (K) and the reciprocal of the power factor (Q) were determined at frequencies of 50, 130, 1,000, and 20,000 kilocycles per second and at 3,000 megacycles per second when K is not greater than 50. At 1 megacycle per second K was determined at temperatures between $-60^$ K and Q were determined at temperatures between 25° and 200° C. The linear thermal ex-
pansion was measured over the temperature range 25° to 700° C. It varied from 0.58 to 0.77 percent. The electrical resistivities of a few specimens were measured at 200° C, using a direct-current potential constantly applied for several days. In some cases the resistivity decreased by a factor of $10⁵$ over a few days. For specimens of some compositions, K and \hat{Q} changed with time.

1. Introduction

Previous studies, by several investigators, of titanate dielectrics have shown that these ceramics are useful in the field of electronic instrumcntation [1 to 5).1 Special applications, such as in some miniature electronic dev ices, necessitate dielectrics in capacitors that will function at elevated temperatures without excessive electrical losses. One of the best insulators at high temperatures is beryllia, and some ceramics containing beryllia are characterized by low electrical losses $[6]$. Despite these facts and the increased interest in titanate ceramics during the past decade, very little information on beryllia-titania dielectrics has been published.

The present paper, dealing with dielectrics composed of beryllia, baria, and titania, is the fourth in a series on ceramic dielectrics made from titania and the oxides of the alkaline earth elements. An ex-
tended range in composition for the system BeO- $BaO-TiO₂$ was covered in this investigation in order to reveal dielectrics that may have desirable properties at various temperatures from -60° to $+200^{\circ}$ C.

II. Preparation of Dielectrics and Methods of Test

Dielectrics having the compositions shown in figure 1 were prepared from reagent quality barium carbonate and beryllia with the commercial grade of titania (grade TMO) used in the preparation of alkaline-earth titanate dielectrics previously investigated [2, 4, 5].

The methods of preparing these dielectrics and of determining their properties have been previously described $[2, 4]$. For measurements of K and Q at 25° to 200° C, the silvered test disk rested on a thin flat silver electrode on a hot-plate, and a silver-wire electrode, in a vertical position, touched the top center of the test disk. These silver electrodes were connected to the terminals on the Q-meter by short lengths (12 in.) of heavy copper wire. Temperatures of the disks on the hot-plate were measured with a calibrated copper-constantin thermocouple $(B&S$ Gage No. 34) inserted into a small bole extending from the edge to the center of a similar disk placed next to the disk being measured. Due to the small thickness (0.1 in.) of the test specimen, the entire piece was maintained within a mall temperature gradient. Tests made on specimens of barium titanate by this procedure gave a Curie point between 115° and 120° C, indicating an accuracy of about $\pm 3^{\circ}$ C.

For electrical leakage tests on capacitors, matured specimens 0.75 in. square by 0.010 in. thick were coated over an area of 2 cm2 on each face with firedon silver electrodes, and silver lead wires were attached. The specimens were heated in an electric furnace, and the temperature was measured on a mercury-in-glass therrnometer placed next to the test piece. Leakage current was measured on a microammeter.

III. Results and Discussion

In table 1, data are given for the composition, heat-treatment, absorption, shrinkage, dielectric constant (K) , and Q -value (reciprocal of the power factor) of mature specimens. The data for a given composition are considered to be the most representative of those obtained from measurements of four to seven specimens.

The effect of composition on the maturing temperature of the specimens is shown in figure 2, in which the specimens having the same maturing tem-
perature are connected by lines. In all cases, the range in temperature within which mature specimens could be produced was not determined, but this range usually was not more than 25° C. Of the 33 bodies with ternary compositions, 25 were matured at 1,275° C, or less, within 1 or 2 hours. Specimens designated BBe63 (table 1) required several heat treatments of 4- to 6-homs duration at 1,315° C to reach maturity. One or more relatively low quin-

¹ Figures in brackets indicate the literature references at the end of this paper

tuple points in the phase diagram for this system are indicated by the low-maturing temperatures over a wide range in composition.

At 1 Mc/s and at 25° C, the variations in values of K and \hat{Q} with composition are shown in figures 3 and 4, respectively. These diagrams were constructed from the data on K and φ given in table 1. In the binary system beryllia-titania, with the substitution of BeO for TiO_2 the values of K decreased from near 100 for $TiO₂$ to 17 for bodies of composition $6BeO:TiO₂$. The observed value of K for $BeO: TiO₂$ was 57, compared to 71 reported by B. M. Wul [7]. The higher values sometimes found are probably due to the presence of small amounts of the lower oxide of titanium, which has a dielectric constant of several thousand. Q-values remained at several thousand until about 50 weight percent of BeO was present. Higher percentages of BeO resulted in specimens with lower Q, which decreased to 130 for $6BeO:TiO₂$. The dielectric constant and Q-values for BeO (99.7 $\%$ pure), matured at 1,925° C and measured at 25° C and 100 kc/s, have been reported as $K=6.3$ and $Q=420$ [6].

Within the ternary system, for dielectrics containing percentages of TiO_2 greater than about 60, the replacement of BaO by BeO did not change the values of K very much, but usually increased the Q -values. However, on the join $3BeO:TiO₂$ - $\mathrm{BaO:2TiO}_{2}$, K decreased from 200 for BaO:2TiO₂ to 30 for 3BeO :TiOz, with a minimum of 25 about midway along the join. The Q-values usually in- creased as the BeO content increased. On the 4BeO :Ti02-2BaO :3TiOz join, *K* decreased rapidly from 900 for $2BaO:3TiO₂$ to 23 for $4BeO:TiO₂$. The addition of 9 weight percent of $4BeO TiO₂$ to $2BaO:3TiO₂$ decreased Q from 50 for $2BaO:3TiO₂$ to 33 for 2BBe49 (table 1), but greater percentages of 4BeO :TiO₂ increased the Q to a maximum of 3,000 at about 90 percent. With more than 90 percent, a decrease in \dot{Q} to 300 for 4BeO:TiO₂ was found. On the $6BeO$:TiO₂-BaTiO₃ join, *K* decreased from about 1,500 for BaTiO₃ to 17 for $6BeO$:TiO₂. Q-values decreased from about 100 for $BaTiO₃$ to 30 when the content of $6BeO$:TiO₂ was 25 percent (BBe67, table 1). Further additions of $6BeO$:TiO₂, increased the Q to a maximum of 8,000 at 90 percent. However, at 100 percent of 6BeO :TiO₂, the Q had decreased to 130.

The effect of variation in frequency on the Q-values may also be noted in table 1. In the large majority of specimens, the Q-values were lower at 50 kc/s than at the higher frequencies. At 20 Mc/s, they were usually higher than at 1 Mc/s for specimens of high titania content, but lower for those of high beryllia or barium titanate content. At $3,000$ Mc/s, higher values of Q were found than at 20 Mc/s for about half of the specimens tested.

In some miniaturized electronic equipment, the parts are subjected to temperatures of about 200° C, necessitating a knowledge of the properties of the dielectrics under these conditions. Data are given, in table 2, for *K* and Q measured at 130 kc/s at temperatures between 25° and 200° C, and for the average temperature coefficient of *K.* These data, in most instances, were obtained on one specimen only of each composition. For most of these dielectrics. K For most of these dielectrics. *K* decreased with increasing temperature, and the average temperature coefficient of K ranged from -35 to -810 ppm/ \degree C. Q-values usually were decreased greatly at higher temperatures, and at 200° C only seven specimens had *Q* greater than 500, with the highest (1,400) for 2BBe8. Only 10 of the 54 test pieces had a higher \mathcal{G} at 200 \degree C than at 25 \degree C. and most of the 10 were of high barium titanate content. The *"Q"* meter was warm and under voltage control of $\pm \frac{1}{2}$ percent when the measurements were made on specimens having a capacitance of 100 to 200 μ ^f. Values of the average temperature coefficient of *K* are probably within ± 20 ppm/^o C. The temperature of the test pieces was raised at the rate of about 3 deg C a minute, and readings were taken at 25 deg C intervals. In order to illustrate the variations in Q resulting from changes in temperature and composition, figures 5 and 6 were constructed for temperatures of 100° and 200° C, respectively, and are based on the data in table 2.

In table 3 data are given for the values of K, at 1 Mc/s, over the temperature range of -60° to $+85^{\circ}$ C and for the average temperature coefficient of *K.* These values were obtained by measuring the capacitance of test disks at 10-deg intervals, with the temperature held constant at each interval for at least 15 min before measurements were made. The average values of the temperature coefficient of *K,* last column of table 3, are considered to be not better than ± 10 ppm/ \degree C, and most of them are negative within the range -40 to -840 ppm/^o C. In order to illustrate the variation of K resulting from changes in temperature and composition, figures 7, 8, and 9 were constructed for temperatures of -60° , $+100^{\circ}$, and $+200^{\circ}$ C, respectively. These figures contain isodielectric-constant lines, based on the data in tables 2 and 3.

After storage for 6 months under room conditions, two or more specimens of each composition were retested for K and Q at 25° C and 1 Mc/s. The results for the dielectrics that showed a significant change are given in table 4. These changes, particularly in K , are not as large, on the average, as those found to occur in the titanate systems previously studied [2, 4, 5]. Specimens of only one composition (BBe69), of high $BaTiO₃$ content, decreased in K and at the same time increased in Q by an appreciable amount. The absence of much solid solution between BeO and $BaTiO₃$ may account for the smaller change, with time, in the electrical properties of these dielectrics compared to those containing the other alkaline-earth oxides.

Linear thermal expansions, determined by the interferometer method, were moderately high for representative specimens, as shown in table 5.

In order to determine the usefulness of these dielectrics in capacitors at 200° C and under a constant potential, tests of the change in electrical resistivity over a period of time were made on some specimens of various compositions. On the assumption that practically all of the conductivity was

through the piece, the approximate volume resistivity was calculated from the amount of current and the dimensions of the test piece between the fired-on silver electrodes. The data obtained are shown in table 6 and figures 10 and 11. Barium titanate specimens showed the fastest and largest decrease in resistivity, while the wafers of high beryllia content showed the least change in resistance. After the tests, only those specimens exhibiting a considerable decrease in resistivity were found to be colored black throughout the volume between the silver electrodes, while portions not under the electrodes remained unchanged in color. This decrease in resistivity and change in color is probably due to the reduction of the tetravalent titanium to the trivalent form. A reversal in the polarity of the applied voltage resulted in a temporary increase in resistivity, indicating a partial reoxidation. The most variable resistivity data were obtained for specimens of barium titanate. One of the factors most likely to influence the resistivity is the number of dark-colored spots in the specimen before the test. The data on barium titanate given in table 6 and figure 10 are the best values for specimens made with a commercial grade of titania. At 200° C and under 3-v direct current per mil, the resistivity for BaTiO₃ is 1.0×10^8 ohmcm when measured immediately after applying the voltage. For the other specimens given in table 6, the resistivity just after application of the voltage is greater than 10^{10} ohm-cm. In order to find how much voltage was needed to cause a decrease in resistivity with time at 200° C, the voltage on specimen BBe67 was increased to 100 (10 y/ml) after the specimen had been at 30 v, and 200° C, for 21 days. The resistivity remained greater than 1010 ohm-cm for 4 additional days and then decreased to 2×10^7 ohm-cm.

The decrease in resistivity shown by these dielectrics, when subjected to a constant voltage, greatly lowers their usefulness for high-temperature duty. Those bodies, however, which showed a small loss in resistivity at 200° C could be used for the production of capacitors for operation at this temperature if the working voltage is not too high.

IV. Summary

Dielectrics having compositions in the system $BeO-BaTiO₃-TiO₂$ can be prepared from mixtures of titania with barium carbonate and beryllia. Mature titania with barium carbonate and beryllia. dielectrics (less than 0.1% absorption) were made by heating specimens to various temperatures within the range $1,240^{\circ}$ to $1,525^{\circ}$ C.

The dielectric constant (K) varied from 16 for specimens with compositions near that of 6BeO:-Ti02, to several hundred for dielectrics of high baria content. Most of the temperature coefficients of K were negative. The Q-values, at 25° C, ranged from 15 to 10,000 and were low for dielectrics containing large percentages of baria and for those with high beryllia content in the binary system BeO-TiO₂. At higher temperatures, most of the Q -values decreased greatly. *K* and Q-values of some of the dielectrics changed with time,

Values for the linear thermal expansion over the temperature range 25° to 700° C, varied from 0.58 to 0.77 percent and were obtained on dielectrics of widely different compositions.

When subjected to an electrical potential at 200° C for many hours, some of the dielectrics decreased greatly in electrical resistivity.

V. References

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FIGURE 1. *Ternary diagram for system BeO-BaTiO₃-TiO₂ <i>showing compositions studied.* $B=BaO$; $Be=BeO$; $T=TiO₂$; thus $Be6T=6BeO$:TiO₂.

FIGURE 2. Approximate maturing temperature (C) after calcining treatment.

 $B = BaO$; $Be = BeO$; $T = TiO₂$.

FIGURE 3. Dielectric constant, at 25° C and 1 Mc/s, with varying composition within the ternary system $BeO-BaTiO₃$ -TiO₂.

FIGURE 4. Q-values, at 25° C and 1 Mc/s, with varying composition within the ternary system BeO-BaTiO₃-TiO₂.

FIGURE 6. Q-values, at 200° C and 130 kc/s, with varying composition within the ternary system BeO-BaTiO₃-TiO₂.

FIGURE 7. Dielectric constant, at -60° C and 1 Mc/s, with varying composition within the ternary system BeO-BaTiO3- $TiO₂$.

FIGURE 8. *Dielectric constant, at 100° C and 130 kc/s, with varying composition within the ternary system₁BeO-BaTiO₃-TiO₂.*

Thickness of all specimens was approximately 0.010 in.

FIGURE 9. Dielectric constant, at 200° C and 130 kc/s, with varying composition within the ternary system BeO-BaTiO₃-TiO₂.

FIGURE 11. *Approximate volume resistivity for specimens of* 5BBe₂, 0.010 in. thick, at 200° C and 110 or 30 volts direct-current, after varying lengths of time.

A, 110 v; B, 30 v; 1, polarity reversed; 2, original polarity restored.

 $\tilde{\mathcal{A}}$

TABLE 2. Dielectric constant (K), Q-values, and average temperature coefficient of K from 25° to 200°C, at 130 kc/s

a Maximum K value occurs between 100° and $125^{\circ}{\rm C}.$

TARLE 3. Dielectric constant, at 1 Mc/s, from -60° to $+85^{\circ}$ C, and average temperature coefficient of dielectric constant

^a Apparent change not significant due to small capacitance of specimen.

TABLE 6. Approximate volume resistivity of some specimens,
0.010 in. thick, measured at 200 $^{\circ}$ C and at a potential of 30-v
direct current maintained for various periods of time

TABLE 5. Linear thermal expansion

 $\,^{\rm a}$ In 2 hr after 2 days, the resistivity began to decrease
Irapidly and, within an additional 2 hr had decreased to
 1×10^5 ohm-cm, when test was discontinued.
 $\,^{\rm b}$ After 7 days.
 $\,^{\rm e}$ After 15 days.

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TABLE 4.

Changes in K and Q of s pecimens after 6 months storage (Measured at 1 Mc/s and 25° C)