(Ladc 2900)
(Full paper)

A STUDY OF PROCESS VARIABLES IN
BARIUM TITANATE CERAMICS.

ABSTRACT

Three commercially available barium titanate powders were employed in this study. These three materials were fabricated into discs suitable for electrical measurements. Several steps in the fabrication process were varied in an attempt to determine optimum conditions for obtaining the best electrical properties for the given material. Calcination, particle size, grinding technique, binder addition, forming method, forming pressure, maturing temperature, firing cycle, cooling cycle, and setter materials were the variables investigated. The effect of these variables on dielectric constant, planar coupling coefficient, density, and firing shrinkage of barium titanate is reported.

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I. Introduction

Work on barium titanate ceramics was begun by Group CMB-6 Ceramics Section of the Los Alamos Scientific Laboratory when this group was requested to fabricate certain pieces of barium titanate which were not readily available commercially. The first step in the program was a literature survey to find what other investigators felt were the recommended ceramic procedures to follow to obtain the best product from a given barium titanate raw material. It was discovered that although the literature on barium titanate is voluminous,¹ the majority of this literature is concerned with the physicists' or electrical engineers' interest in the end product. There are few papers² concerned with the majority of variables a ceramic engineer would encounter in his attempts to produce a good barium titanate ceramic. Therefore, the purpose of this work was to investigate the various ceramic parameters in processing barium titanate ceramics to determine the best procedure to use in preparing barium titanate ceramics from a given raw material.

II. Experimental Procedure

A. Ceramic Processing:

Three different batches of commercial barium titanate of the best available purity were used in this investigation. These three batches were designated as A, B, and C for sample numbering purposes. Three different materials were used because small batches of these were on hand. Table I lists the samples and the ceramic processing for each.

TABLE I

<u>Sample</u>	<u>Description</u>
A-1	Material as-received mixed with 3 w/o binder, pressed into discs at 20,000 psi, fired to 1250°C with 4 hour soak.
A-2	Same as A-1 except pressed at 10,000 psi.
A-3	Same as A-1 except fired to 1350°C with 4 hour soak.
A-4	Same as A-3 except pressed at 10,000 psi.
A-5	Same as A-1 except fired at 1450°C with 4 hour soak.
A-6	Same as A-5 except pressed at 10,000 psi.
A-7	Material as-received mixed with 3 w/o binder, pressed at 10,000 psi into briquettes, calcined at 1350°C, ground in mortar and pestle to -35 mesh, pulverized to -60 mesh, mixed with 3 w/o binder, pressed at 10,000 psi into discs, and fired to 1500°C with 4 hour soak.
A-9	Same as A-7 except fired to 1550°C with 4 hour soak.
A-10	Same as A-8 except fired to 1550°C with 4 hour soak.
A-11	Material as-received fused at 1650°C in Pt dish in gas-air furnace, ground in mortar and pestle, milled 10 hours to an average particle size of 1.84 μ , dried, ignited at 300°C for 24 hours, mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired to 1450°C with 4 hour soak.
A-12	Same as A-6 except fired to 1450°C with no soak.
A-13	Same as A-6 except fired to 1450°C with 1 hour soak.
A-14	Same as A-6 except fired to 1450°C with 2 hour soak.
A-15	Same as A-6 except fired to 1450°C with 3 hour soak.
A-16	Same as A-11 except ignited at 500°C for 24 hours.

TABLE I (Cont.)

<u>Sample</u>	<u>Description</u>
A-17	Material as-received milled 10 hours to an average particle size of $1.07\ \mu$, dried, ignited at 500°C for 24 hours, mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired at 1450°C with no soak.
B-1	Material as-received mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired to 1450°C with 4 hour soak.
B-2	Material as-received pulverized to -100 mesh, mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired at 1450°C with 4 hour soak.
B-3	Material as-received milled 10 hours to an average particle size of $3.25\ \mu$, dried, ignited at 500°C for 24 hours, mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired to 1450°C with 4 hour soak.
B-4	Material as-received milled 21-1/2 hours to an average particle size of $2.84\ \mu$, dried, ignited at 500°C for 24 hours, mixed with 1-1/2 w/o binder, tamped into a cylindrical rubber sack, hydrostatically pressed at 30,000 psi, discs cut from the pressed cylinder, and fired at 1450°C with no soak.
B-5	Same as B-4 except a vacuum pulled on the rubber sack before pressing.
B-6	Material as-received milled 36 hours to an average particle size of $2.11\ \mu$, dried, ignited at 500°C for 24 hours, mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired to 1450°C with no soak.
B-7	Same as B-6 except fired on ZrO_2 setter.

TABLE I (Cont.)

<u>Sample</u>	<u>Description</u>
B-8	Same as B-6 except fired on Al_2O_3 setter.
B-9	Same as B-6 except fired on MgO setter.
B-10	Same as B-6 except after firing, cooled at 50°C/hr to 600°C and then furnace cooled.
B-11	Same as B-6 except fired at 1450°C with 1 hour soak, cooled at 50°C/hr to 1200°C , soaked at 1200°C for 4 hours, cooled at 50°C/hr to 500°C , and then furnace cooled.
B-12	Material as-received milled 47 hours to an average particle size of $1.49\ \mu$, dried, ignited at 500°C for 24 hours, mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired at 1450°C with no soak.
B-13	Same as B-12 except not ignited.
C-1	Material as-received milled 22-1/2 hours to an average particle size of $2.97\ \mu$, dried, ignited at 500°C for 24 hours, mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired to 1460°C with 1 hour soak.
C-2	Same as C-1 except fired to 1460°C with no soak.
C-3	Same as C-1 except after firing, cooled at 50°C/hr to 600°C and then furnace cooled.
C-4	Same as C-1 except after firing, cooled at 50°C/hr to 1200°C , soaked at 1200°C for 4 hours, cooled at 50°C/hr to 500°C and then furnace cooled.
C-5	Material as-received milled 48 hours to an average particle size of $2.33\ \mu$, dried, ignited at 500°C for 24 hours, mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired at 1460°C with 1 hour soak.

TABLE I (Cont.)

<u>Sample</u>	<u>Description</u>
C-6	Material as-received milled 62 hours to an average particle size of 1.41 μ , dried, ignited at 500°C for 24 hours, mixed with 1-1/2 w/o binder, pressed at 10,000 psi, into discs, and fired at 1460°C with one hour soak.
C-7	Same as C-6 except fired at a rate of 200°C/hr to 1460°C, soaked one hour at 1460°C, and furnace cooled.
C-8	Same as C-6 except fired at a rate of 100°C/hr to 1460°C, soaked one hour at 1460°C, and furnace cooled.
C-9	Same as C-6 except fired at a rate of 50°C/hr to 1460°C, soaked one hour at 1460°C, and furnace cooled.
C-10	Same as C-6 except fired to 1460°C, soaked one hour at 1460°C, cooled at 100°C/hr from 1460°C to 500°C, and then furnace cooled.
C-11	Same as C-6 except fired at a rate of 100°C/hr to 1460°C, soaked one hour at 1460°C, cooled at 100°C/hr from 1460°C to 500°C, and then furnace cooled.
C-12	Same as C-6 except fired at a rate of 100°C/hr to 1200°C, soaked 4 hours at 1200°C, fired 100°C/hr to 1460°C, cooled at 100°C/hr to 500°C and then furnace cooled.
C-13	Same as C-6 except low-fired to 1000°C in an electrical resistance furnace, high-fired at 1460°C with 1 hour soak in an induction furnace at a rate of R.T. to 1460°C in 1/2 hour, and furnace cooled.
C-14	Same as C-6 except prefired to 1400°C with a flush of air introduced in the kiln throughout the firing cycle, and then refired at 200°C/hr to 1460°C with 1 hour soak.

TABLE I (Cont.)

<u>Sample</u>	<u>Description</u>
C-15	Material as-received milled to an average particle size of 1.66 μ , dried, mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired as was C-14.
C-16	Same as C-15 except 1-1/2 w/o water used in place of the organic binder.
C-17	Material as-received milled to an average particle size of 3.66 μ dried, mixed with 1-1/2 w/o binder, pressed at 10,000 psi into discs, and fired at 1460°C with 1 hour soak.

1. Particle Size Reduction.

Average particle size of the as-received barium titanate powder was: material "A", 1.17 μ ; material "B", 35 μ ; and material "C", 34 μ . The particle size reduction was achieved by use of a standard laboratory chemical porcelain mortar and pestle, a pulverizer, and/or a polyethylene lined ball mill. This mill and the barium titanate balls used in it are illustrated in Figure 1. The mill charge was 2000 grams 1 inch diameter balls, 1000 grams 1/2 inch diameter balls, 300 cc distilled water, and 1000 grams barium titanate powder. Ball loss during milling was 1 to 2% and mill lining loss was negligible ($\sim$ 0.5%) after the lining was "worn in" and less than 1.5% before this. Barium titanate balls were fabricated by mixing as-received material with 3 w/o binder, pressing the material at 10,000 psi in a steel die to obtain the desired configuration, and firing the balls in a zirconia crucible in a gas-air furnace to 1500°C with no soak at peak-temperature.

2. Drying and Ignition.

Both drying and ignition were carried out by placing the material in porcelain evaporating dishes. The material was dried in a convection type dryer at 100°C for 24 hours, and ignited in an electrical resistance type furnace at 300 or 500°C for 24 hours.

3. Pressing.

Discs having dimensions of 3/4 inch diameter by 1/8 inch thick before firing were made for electrical testing purposes. Except for samples B-4 and B-5 these discs were all prepared by standard dry pressing techniques. The binder used throughout this investigation was Carbowax PF 4000 (a Carbide and Carbon Chemicals product). The procedure followed for introducing the binder was to melt the desired weight of binder in a beaker, dissolve

O-RING

POLYETHYLENE

DURAL

POLYETHYLENE LINED BALL MILL AND BaTiO_3 BALLS

Fig. 1

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the melt in carbon tetrachloride, blend this solution with the barium titanate powder by hand mixing, and evaporate the carbon tetrachloride from the mix in a chemical fume hood.

Samples B-4 and B-5 were prepared by standard hydrostatic pressing techniques. The cylinders obtained from this process were turned down on a lathe to 3/4 inch diameter. Discs were cut from this cylinder and faced off on 400 grit emery paper to 1/8 inch thickness.

4. Firing.

The majority of the firings were done in a full muffled silicon carbide resistance element kiln. This unit was controlled by a 24 hour cam type program controller. The controller temperature was calibrated by placing a Pt-Pt 10% Rh thermocouple on the furnace floor adjacent to the sample being fired. The controller temperature and thermocouple temperature were found to agree within $\pm 5^{\circ}\text{C}$. Where no firing or cooling cycle is given in Table I, the furnace was allowed to reach temperature and to cool at its own uncontrolled rate. Furnace firing rate was approximately $300^{\circ}\text{C}/\text{hour}$ and its cooling rate down to 500°C was approximately $150^{\circ}\text{C}/\text{hour}$. Platinum discs 0.020 inch thick were used for setters in every firing except for samples B-7, B-8 and B-9. In these instances 1/8 inch thick discs of ZrO_2 , Al_2O_3 and MgO were used as setters. The samples were fired in direct contact with the setter.

The gas-air furnace employed was a small pot type about 19 inches O.D., 9 inches I.D. and 30 inches tall with a full muffle. Temperatures were determined with an optical pyrometer sighted on the muffle. As noted in Table I, sample C-14 was low fired in an electrical resistance type furnace. This step was introduced to remove the binder and sinter the sample sufficiently in order that it could be fired rapidly in the induction coil.

Figure 2 illustrates the induction firing set-up. The platinum discs separating the samples acted as the susceptor and temperatures were determined with an optical pyrometer sighted on the top platinum disc. The air flush mentioned for samples C-14, C-15, and C-16 was simply a tube from a compressed air source thrust through the furnace door with the air introduced at 18 psi.

B. Ceramic Tests:

Density and firing shrinkage measurements were the two ceramic tests made on the samples.³ The results are reported in Table II and represent the average of 3 samples.

The firing shrinkage reported was actually overall shrinkage and was calculated from the following formula:

$$100 \times \frac{\text{Die Diameter-Fired Diameter}}{\text{Fired Diameter}} = \% \text{ Firing Shrinkage} \quad (1)$$

Density was obtained by weighing the samples dry, boiling them 2 hours in distilled water, weighing them saturated, and weighing them suspended in water. Calculations were based on the following formulae:

$$\frac{\text{Saturated Weight-Suspended Weight}}{\text{Density of Water}} = \text{Volume} \quad (2)$$

$$\frac{\text{Dry Weight}}{\text{Volume}} = \text{Bulk Density} \quad (3)$$

A check on the above method was accomplished using carbon tetrachloride instead of water and boiling 5 hours instead of 2 hours. The density figures obtained were identical in both cases. Some investigators⁴ have reported barium titanate to be hygroscopic, hence the reason for the carbon tetrachloride check method.

C. Electrical Tests:

Relative dielectric constant (K) and planar coupling coefficient (K_p) were the two electrical properties measured in this investigation, and the

INDUCTION FIRING OF BaTiO₃ SAMPLES

985-12

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TABLE IX

Sample	Firing Shrinkage %	Density gm/cc	Relative Dielectric Constant, K	Planar Coupling Coefficient, K_p
A-1	12.5	5.19	1039	0.194
A-2	13.3	5.13	1042	0.240
A-3	15.4	5.51	1678	0.340
A-4	15.7	5.54	1680	0.340
A-5	15.1	5.54	1742	0.389
A-6	17.8	5.54	1742	0.390
A-7	16.0	5.46	1657	0.397
A-8	4.4	4.96	1792	0.306
A-9	12.8	4.99	1372	0.361
A-10	5.4	5.17	1158	0.334
A-11	15.8	5.47	1920	Shorted
A-12	19.2	5.52	1740	0.360
A-13	19.4	5.54	1580	0.326
A-14	18.8	5.44	1540	0.312
A-15	18.3	5.72	1937	0.344
A-16	13.7	5.55	1900	0.358
B-1	5.3	4.49	1140	Shorted
B-2	3.1	4.62	1000	Shorted
B-3	12.1	5.67	1600	0.346
B-4	13.0	5.56	1750	0.352
B-5	12.6	5.68	1790	0.270
B-6	14.1	5.73	1880	0.351
B-7	14.4	5.74	1880	0.351
B-8	14.7	5.73	1835	0.330

TABLE II (Cont.)

<u>Sample</u>	<u>Firing Shrinkage %</u>	<u>Density gm/cc</u>	<u>Relative Dielectric Constant, K</u>	<u>Planar Coupling Coefficient, K_p</u>
B-9	14.2	5.72	1800	0.365
B-10	14.0	5.70	1880	0.354
B-11	14.2	5.74	1925	0.310
B-12	15.7	5.64	1690	0.313
B-13	16.0	5.66	1710	0.313
C-1	13.4	5.46	2260	0.360
C-2	12.5	5.46	1480	0.246
C-3	13.3	5.65	1423	0.338
C-4	13.2	5.60	1476	0.312
C-5	13.4	5.62	1765	0.313
C-6	16.1	5.66	1570	0.254
C-7	13.7	5.65	1827	0.325
C-8	13.8	5.66	1972	0.340
C-9	13.3	5.64	1732	0.339
C-10	13.1	5.62	1764	0.318
C-11	13.4	5.61	1765	0.332
C-12	13.5	5.64	1820	0.328
C-13	13.8	5.61	1771	0.270
C-14	15.8	5.63	2150	0.347
C-15	16.2	5.68	1845	0.362
C-16	14.9	5.72	1880	0.348
C-17	6.1	4.92	1000	0.260

results are reported in Table II. A total of three samples were tested and averaged for each value reported.

The samples were lapped plane and parallel before electroding. The samples were electroded by painting on silver paste (DuPont 4822), which was then fired in air at 730°C. The samples were poled by heating them above the Curie temperature (120°C) in Silicone 200 oil and applying a field of 30 KV/inch thickness across the samples. After poling, they were cooled to 70°C in 10 minutes and then to room temperature at an uncontrolled rate.

The resonant frequency, anti-resonant frequency, and capacitance were measured by standard techniques⁵ 48 hours after polarization. The capacitance was measured at one kilocycle. From these values it was possible to calculate K and K_p .⁵

III. Discussion of Results:

The data obtained in this investigation is tabulated in Table II. A portion of this data has been graphically illustrated in Figures 3 through 9.

As may be noted in Table I, the samples fabricated of material "A" were prepared in order to study firing temperature and time at temperature, forming pressure, effects of calcining and fusing, and ignition temperature.

Samples A-2, A-4, and A-6 were fired at 1250°C, 1350°C, and 1450°C respectively with 4 hours soak at temperature. Figure 3 illustrates the effect of firing temperature on K and K_p , and it is apparent that 1450°C is the best firing temperature of these three temperatures. Also, the slopes of these curves indicate that higher firing temperatures would yield little gain in values of K and K_p .

On the assumption that 1450°C was the best firing temperature, samples A-12, A-13, A-14, A-15, and A-16 were made and fired at 1450°C with soaks

EFFECT OF FIRING
TEMPERATURE ON RELATIVE DIELECTRIC
CONSTANT AND PLANAR COUPLING COEFFICIENT

Fig. 3

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at temperature of 0, 1, 2, 3, and 4 hours respectively. Figure 4 shows that a soak at temperature of either zero or 4 hours is the best of these soaking times, and that perhaps a greater time than 4 hours would give higher K and K_p values. The high K and K_p values with the 4 hour soak are somewhat difficult to accept since soaks of 1, 2, and 3 hours yielded progressively lower values. This whole series of samples should be repeated to confirm the somewhat anomalous results. However, the trend appears to be established.

The firing time and temperature employed for materials "B" and "C" were based on the results obtained for material "A". Material "B" was fired to 1450°C with no soak as was found best for material "A"; this was apparently satisfactory (see Table II, samples B-4 through B-13). A firing temperature of 1460°C with 1 hour soak was found best for material "C", as seen in Table II by a comparison of Sample C-1, 1 hour soak, to sample C-2, no soak.

Figures 5 and 6 are graphical illustrations of the results of calcining and fusing studies on material "A" which include samples A-7 through A-11 and A-16. Sample A-6 is illustrated to give some comparison to as-received material. The assumption is made that if this sample were fired at 1500°C for 4 hours soak, its K and K_p values would be little different. It would be well to note here, as seen in Figures 5 and 6, that high K values are not necessarily associated with high K_p values and vice versa.

A study of Figure 5 indicates that for a high K value, fusion of the raw material is advantageous over calcination or use of as-received material, and 1500°C is a better firing temperature than 1550°C. One variable not taken into account here was the average particle size of the material in each instance, except for A-6, A-11, and A-16. The shrinkages and densities for A-8 and A-10 indicate their particle sizes were probably too great for producing good bodies. Samples A-11 and A-16 had average particle sizes

EFFECT OF SOAKING TIME
AT TEMPERATURE ON RELATIVE DIELECTRIC
CONSTANT AND PLANAR COUPLING COEFFICIENT

Fig. 4

493-18

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EFFECT OF PREREACTION ON RELATIVE DIELECTRIC CONSTANT

Fig. 5

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PLANAR COUPLING COEFFICIENT

.300 .325 .350 .375 .400

EFFECT OF PREREACTION ON PLANAR COUPLING COEFFICIENT

Fig. 6

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only a little larger than that of A-6 (1.84 u vs 1.17 u), and A-11 and A-16 were fired at the same temperature for the same length of time as A-6. Samples A-11 and A-16 had somewhat greater K values than A-6, but as will be brought out later, the reason may have been particle size rather than fusion of the material. The shrinkages and densities of A-7 and A-9 indicate their average particle sizes were probably small enough to yield good bodies, but their K values show little gain over uncalcined material such as was used for A-6.

Figure 6 indicates that use of as-received material will give nearly as high a K_p value as either calcined or fused material. Sample A-7, calcined, does have the highest K_p of these samples, indicating some value for the calcining process.

It should be noted that A-11 shorted during poling and could not be poled. Chemical analysis of this sample disclosed 100 ppm of carbon present, which it was felt accounted for the shorting. The carbon was thought to have come from the mill liner so in preparing A-16, ignition temperature was increased to 500°C. Evidently this solved the problem because A-16 poled readily. After a dozen or more runs with the mill, the ignition step was eliminated with no harmful effects. See samples B-12 and B-13, Table II. The mill liner was "worn in" by this time and mill liner pick-up was negligible. On the subject of shorting during poling, samples B-1 and B-2 shorted and this anomaly could not be resolved by the carbon pick-up solution. The only solution offered here was the poor quality of the samples as evidenced by the low values of density, shrinkage, and K.

Figure 7 illustrates the effect on K and K_p values of firing barium titanate on various setter materials. Platinum was the best setter material for obtaining both good K and K_p values. Use of a zirconia setter yielded

SAMPLES FIRED AT 1450 °C WITH NO SOAK

EFFECT OF SETTER MATERIAL ON RELATIVE DIELECTRIC CONSTANT AND PLANAR COUPLING COEFFICIENT

Fig. 7

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the highest K value but only the third best K_p value, whereas the magnesia setter yielded the second highest K_p value and the lowest K value. Visual inspection of the samples after firing showed some reaction between alumina and barium titanate, and magnesia and barium titanate; but none between platinum and barium titanate, and zirconia and barium titanate. A spectrochemical analysis of the samples revealed no pick-up of the setter constituents in the samples after firing. If the samples were fired with barium titanate grog separating them from the setter, any of the setter materials mentioned could probably be used, with zirconia or platinum being the most desirable. Of course, a setter made of barium titanate would undoubtedly be very good.

A series of samples, C-6, C-7, C-8, and C-9, were prepared in the same manner except for varying the firing cycle. The graph of the results of the different firing cycles, Figure 8, shows that a rate of about 100°C per hour on the heating cycle appears to yield the best values of K and K_p .

Several other variations in the firing procedure were made. Sample C-10 was prepared and fired identically as was sample C-6 except a controlled cooling rate of 100°C per hour was employed. The results in Table II show that the controlled cooling rate resulted in improved K and K_p values. However, sample C-11 differed from C-8 in the same manner as C-10 differed from C-6, but in this case (C-11 vs C-8) the controlled cooling rate lowered the K and K_p values. Since the firing cycle of 100°C per hour heat up and furnace cool was found to be the optimum, it seems logical to assume that slower cooling cycle will not aid the K and K_p of a properly fired sample.

Sample C-12 was prepared and fired identical to C-11 except during heating C-12 was soaked 4 hours at 1200°C. This resulted in a slight gain in K and slight loss in K_p values for C-12 over C-11.

PEAK TEMP 1460°C with 1 hour SOAK

EFFECT OF FIRING RATE ON RELATIVE DIELECTRIC CONSTANT AND PLANAR COUPLING COEFFICIENT

Fig. 8

99-3-24

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Sample C-13, prefired to 1000°C, was rapidly fired to maturing temperature, soaked 1 hour at temperature, and cooled rapidly in an induction coil, resulting in a gain in both K and K_p over these same values for C-6.

A variation in preparing sample C-14 over sample C-7 was to prefire C-14 to 1400°C with the furnace flushed with air during the firing and cooling cycle. The result was an increase in K and K_p over the values obtained for C-7. This was somewhat to be expected as most ceramics are improved by firing in a good oxidizing atmosphere.

Samples C-1, C-3, and C-4 were prepared to study the effects of varied cooling procedures on resultant K and K_p values. Sample C-1 was allowed to furnace cool after firing, C-3 was cooled at 50°C per hour, and C-4 was cooled at 50°C per hour except held 4 hours at 1200°C. The furnace cooled sample had the highest K and K_p values of these three samples, C-3 had the lowest K , and C-4 had the lowest K_p .

Cooling cycle studies were run also on material "B"; samples B-6, B-10, and B-11. Sample B-6 was furnace cooled after firing to 1450°C with no soak and B-10 was identical except that it was cooled at 50°C per hour from peak temperature to room temperature. The controlled cooling gave a slightly higher K value and a lower K_p value. Sample B-11 was identical to B-10 except it was soaked 1 hour at 1450°C and soaked 4 hours at 1200°C on the cooling cycle. A higher K value and lower K_p value over that of B-10 were obtained in this manner.

For a given firing temperature it was found that K and K_p vary according to the average particle size of the starting material. This effect is illustrated in Figure 9. It is seen that an average particle size of approxi-

EFFECT OF AVERAGE PARTICLE
SIZE OF STARTING MATERIAL ON RELATIVE DIELECTRIC
CONSTANT AND PLANAR COUPLING COEFFICIENT

Fig. 9

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ately three microns yields the best K and K_p for a firing of 1460°C with 1 hour soak. A comparison of sample A-12, average particle size $1.17\ \mu$, to sample A-17, average particle size $1.07\ \mu$, shows an appreciable gain in K with smaller particle size and a slight lowering in K_p . With material "B", results were similar to those of material C in that B-6, average particle size $2.11\ \mu$, had a slightly lower K and a greater K_p than B-12, average particle size $1.49\ \mu$.

A brief study was made on the effect of forming pressure on K and K_p and it was found that between samples pressed at 10,000 psi and 20,000 psi there was little difference in K and K_p . The results for A-1 through A-6 in Table II bring this out.

Hydrostatic pressings at 30,000 psi were made with samples B-4 and B-5. These samples had an average particle size of $2.84\ \mu$ as compared to B-6 which had an average particle size of $2.11\ \mu$. If the results of Figure 10 are accepted, the $2.84\ \mu$ size should have given a better sample. However, the results in Table II show that the samples hydrostatically pressed had both lower K and K_p values than sample B-6 which was dry pressed at 10,000 psi.

It was felt that the organic binder used in preparing most of the samples might be detrimental to electrical properties. Therefore samples C-15 and C-16 were prepared; C-15 with the organic binder and C-16 with water as the binder. The data in Table II shows C-16 to have a higher K and a lower K_p than C-15.

A study of the data in Table II reveals that samples with the higher densities do not necessarily possess the higher K and K_p values. The highest K value obtained was 2260 and this sample, C-1, had a density of $5.46\ \text{g/cc}$.

The highest K_p was 0.397 for sample A-7 which had a density of 5.46 gm/cc. The highest density was 5.74 gm/cc for samples B-7 and B-11 which respectively had K values of 1880 and 1911 and K_p values of 0.351 and 0.310. From the data of Table II it is seen that good electrical properties are generally obtained when a density of 5.40 gm/cc or greater is attained.

IV. Conclusions:

While it is apparent that this study was not a complete treatment of all the ceramic parameters involved in producing barium titanate ceramics, it is felt that a sufficient number of these parameters was considered to draw some basic conclusions with respect to optimum conditions for producing barium titanate ceramics. These conclusions are listed below.

A. For a given raw material the best maturing temperature and time at temperature are the shortest possible time at a temperature just high enough to give complete vitrification. In general, this would probably be approximately 1450°C for zero to one hour soak. Some investigators⁶ feel temperatures much above 1450°C may lead to formation of the undesirable hexagonal phase of barium titanate.

B. A heating rate of approximately 100°C per hour up to temperature and then cooling at least as fast as natural furnace cooling seems to be the best firing procedure.

C. The atmosphere should be oxidizing during firing with an excess of air or oxygen introduced into the furnace during firing to insure oxidizing conditions.

D. Probably the best setter material to use during firing is either platinum or barium titanate with zirconia also being satisfactory.

E. Prereaction such as calcining or fusing of commercially available barium titanate appears to yield little gain in electrical properties.

F. Forming pressures greater than 10,000 psi are of little value in achieving higher K and K_p values.

G. Use of an organic binder during dry pressing which will burn out readily during firing appears to have no detrimental effects on K and K_p .

H. A starting material with an average particle size of approximately 3 μ is most desirable for obtaining high K and K_p values from barium titanate fired in the 1450°C region. Material with an average particle size greater than 3 μ seems too unreactive in this temperature region but might prove satisfactory at higher maturing temperatures.

I. A desirable method to achieve particle size reduction of raw materials with minimum contamination is use of a ball mill lined with an organic material and grinding media of barium titanate. The organic material should be one that can readily be burned out of the milled raw material.

Although the above conclusions were based on a cumulation of results obtained from three different raw materials, the authors feel that the study was sufficiently comprehensive that the same conclusions would have been drawn had only one material been used throughout the investigation.

Plans for future study on barium titanate by the authors include producing a barium titanate ceramic employing all the "desirable" conditions indicated from this study.

Acknowledgements

The authors wish to sincerely thank the following people for their valuable contributions to this investigation: Robert Caird, Vernon Johnson, Edward Shunk, and Robert Wagner, who performed all the electrical testing; Bettie Shroyer who helped immensely in the literature survey and abstracted many articles; Joe Maestas, who performed all the ceramic technician work in preparing and firing the samples and measured the shrinkages and densities; and Denton Dohl and Robert Cowan for their valuable comments in preparation of the manuscript.

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