

UNCLASSIFIED

AD NUMBER
AD401220
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; JAN 1963. Other requests shall be referred to Army Signal Research and Development Laboratory, Fort Monmouth, NJ.
AUTHORITY
USAFE ltr, 1 May 1965

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD 401 220

*Reproduced
by the*

**ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA**



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Abstract

This report describes work done during the third quarterly contract period for the project "Ultra-Fine Particle Size Ferroelectrics", which is directed to the preparation of controlled fine-grained dielectric films; and also to theoretical studies of the phenomena associated with the discontinuities in electrical properties which occur when the particle size of ferroelectric materials is reduced below certain levels.

During this program period, a study of the grain growth inhibition of fine-particled, substantially pure barium titanate ceramics was extended, employing the technique of depositing tantalum (V) from a solution of tantalum oxalate, on to the surface of the barium titanate particles. This method was so effective that the deliberate controlled introduction of a sintering contaminant was found necessary to facilitate densification at temperatures below the melting point of the bulk material.

A correlation was established between inhibitor concentration and terminal grain size of the fired ceramic, somewhat independent of the starting particle sizes, so that ceramic bodies of predetermined grain size larger than 2000A°, could be obtained, even using "extended" firing schedules. In the smallest grain sizes, the Curie point was found to have been eliminated from the temperature range measured.

A method was developed for producing a mixed calcium barium titanate of high purity, and of particle size approaching 100A°, by the pyrolysis of an intermediate mixed oxalate.

Preliminary experiments have been performed to ascertain the feasibility of depositing barium titanate in films by reactions in situ between soluble organic barium salts and titanium acylates in organic media. However, it was found that



the formation of intermediate gel phases restricted the development of coherent films of barium titanate, although these reactions were found to produce barium titanate in bulk systems.

Work was continued on the precipitation synthesis of barium titanate, with a view to increasing batch sizes and checking the reproducibility of the particle size and stoichiometry. Certain technical difficulties were encountered in the recovery process which limited direct scaling up of the synthesis of 100A° average particle sizes, without extensive modifications in the laboratory procedure.



TABLE OF CONTENTS

	<u>PAGE</u>
Abstract.....	i
Table of Contents.....	iii
List of Tables.....	iv
List of Figures.....	v
1. Grain Growth Inhibition Studies.....	1
1.1 Control of Densifications by Sintering Aids.....	1
1.2 Use of Tantalum Oxide to Inhibit Grain Growth.....	2
1.3 Electrical Properties of Barium Titanate Ceramics with Controlled Grain Growth.....	9
2. Mixed Titanates In Ultra-Fine Particle Sizes Derived from the Pyrolysis of the Oxalates.....	17
2.1 Background.....	17
2.2 Experimental Methods.....	17
3. Ultra-Fine BaTiO ₃ by the Precipitation Technique.....	20
3.1 Objectives.....	20
3.2 Reproducibility Experiments.....	20
3.3 Effect of the Recovery Process in the BaTiO ₃ Ratio.....	21
3.4 Scaling Up.....	23
3.5 Densification of Ultra-Fine BaTiO ₃	23
4. Precipitation of BaTiO ₃ Films from Homogeneous Solution.....	24
Program for the Next Contract Period.....	26
List of References.....	27



LIST OF TABLES

<u>TABLE NO.</u>		<u>PAGE</u>
I	Effect of SiO_2 on Sinterability of High Purity BaTiO_3	2
II	Effect of Tantalum Oxide on Grain Growth of BaTiO_3 Ceramics.....	3
III	Breakdown Fields of Inhibited Grain Size BaTiO_3 Ceramics.....	16
IV	Reproducibility of Controlled Size BaTiO_3 by the Precipitation Techniques.....	20
V	Effect of the Recovery Process on the BaO/TiO_2 Ratio.....	22



LIST OF FIGURES

<u>FIGURE NO.</u>		<u>PAGE</u>
1(a),(b)	Effect of Ta_2O_5 Content on Grain Growth of $BaTiO_3$ Ceramic.....	6,7
2	Electron Micrographs of Ceramic $BaTiO_3$ with Ta_2O_5 Added.....	8
3	Electrical Properties of $BaTiO_3$ Bodies with Average Grain Size 1.0 Micron.....	10
4	Electrical Properties of $BaTiO_3$ Bodies with Average Grain Size 0.2 Micron.....	11
5	Electrical Properties of $BaTiO_3$ Ceramic with Average Grain Size 40 Micron.....	12
6	Hysteresis Loops of $BaTiO_3$ Bodies with Average Grain Size 1.0 Micron.....	13
7	Hysteresis Loops of $BaTiO_3$ Bodies with Average Grain Size 0.2 Micron.....	14
8	Hysteresis Loops of $BaTiO_3$ Ceramic with Average Grain Size 40 Micron.....	15



1. GRAIN GROWTH INHIBITION STUDIES

1.1 Control of Densification by Sintering Aids.

The initial experiments performed on firing high purity stoichiometric barium titanate materials to produce high density ceramics employed the flash firing technique in order to restrict grain growth. It was found that with starting particle sizes of about 1μ , using C. P. grade BaTiO_3 , it was impossible to achieve densifications greater than 90%, without suffering the large grain sizes (greater than 30 microns), which accompanied the use of a higher temperature or extended time.

On the other hand, using the lower purity capacitor grade BaTiO_3 facilitated the attainment of a 95% densification level, with grain growth factors of only about 2.5.

The following approach was therefore adopted. High purity BaTiO_3 was deliberately contaminated by the addition of substances which are known to form eutectics with it. The contaminants were added by deposition on the surface of the BaTiO_3 particles, since it was felt that this technique would constitute a more efficient aid to sintering than a calcination method; also, the very small amounts of contaminant necessary would not effect the electrical properties of the ceramic that depend on the geometry of the crystal lattice.

Preliminary experiments attempted to employ ZrO_2 as a sintering aid. This was deposited on the surface of the barium titanate particles by tritulating BaTiO_3 materials (obtained by pyrolysis of the oxalate) with a solution of zirconyl acetate, using the equivalent of 0.8 mole percent ZrO_2 .

The powder was pressed into pellets, baked out 15 minutes at 1500°F to decompose and volatilize the organic residues, and finally sintered at temperatures at

which appreciable densification occurred. Using shrinkage and density measurements to estimate densification, it was found that the use of ZrO_2 did not enhance sinterability to any measurable degree.

Subsequently, silica was applied in the same manner, except using an ammonia-stabilized colloidal solution of SiO_2 (Ludox AS), in amounts corresponding to only 0.12 mole percent. Since, as is well known, the presence of a vitreous phase is extremely detrimental to the dissipation factors of titanate ceramics, the concentration of SiO_2 was deliberately minimized. A study of phase stabilities in the system $BaTiO_3-SiO_2$ (1) indicates that glasses are unlikely to exist in ranges of composition which might be present at the grain boundaries. Also, commercial grades of $BaTiO_3$ commonly contain up to 0.2 mole percent of SiO_2 .

Using 0.12 mole percent silica yielded substantial improvements in sinterability; see Table I.

TABLE I

Effect of SiO_2 on Sinterability of High Purity $BaTiO_3$

<u>Material</u>	<u>Firing Schedule</u>	<u>Shrinkage</u>	<u>Densification</u>
$BaTiO_3$ obtained by pyrolysis of oxalate at 1800°F	1 minute at 2300°F	8.8%	60%
Same as above + 1/2 weight percent SiO_2	"	15.9%	86%

Dissipation factors were found to be unaltered by the presence of the silica, when compared with those of a control to which no silica was added.

1.2 Use of Tantalum Oxide to Inhibit Grain Growth.

A study was made on the effect of tantalum oxide using 0.12 mole percent silica to promote sintering, and amounts of a tantalum oxalate solution equivalent to

0.125 to 2.5 weight percent of Ta_2O_5 . The general method of preparing the specimens was as follows: The powders were trituated with a water solution containing the calculated amounts of Ludox AS colloidal silica, mixed with a freshly centrifuged stock solution of tantalum oxalate (Kawecki Chemical Company). After air drying several hours, the powder was pressed into disks at 8000 psi, with no binder added. Following a 15 minute bakeout, the specimens were given a 20 minute extended firing at 2750°F, using the procedure described in the previous quarterly report of this project.

Table II illustrates the results obtained with various additions of Ta_2O_5 , using different starting particle sizes of barium titanate, derived from the pyrolysis of barium titanyl oxalate at different temperatures. 0.12 mole percent of SiO_2 was added in each case to facilitate sintering.

Percent open porosity was determined by weighing the densified specimen before and after placing in boiling water for 15 minutes; grain sizes were measured using methods detailed in the last quarterly report for this project.

TABLE II

Effect of Tantalum Oxide on Grain Growth of $BaTiO_3$ Ceramics + 1/2% SiO_2

<u>Average Starting Particle Size, μ</u>	<u>% Ta_2O_5</u>	<u>% Densification</u>	<u>% Open Porosity</u>	<u>Average Grain Size, μ</u>	<u>Average Grain Growth Factor</u>
0.4	1.25	94.2	1.5	0.8	2
0.4	0.5	93.7	0.0	1.0	2.5
0.4	0.125	90.0	0.0	4.0	10.
0.2	2.5	95.8	0.0	0.2	1.5
0.2	1.0	89.6	0.0	0.5	2.5
0.2	0.25	72.5	12.5	6.0	30.
0.09	2.0	100.	0.0	0.3	3.3
0.09	0.5	85.	0.0	1.5	17.

It is evident from Table II that the average grain size of the fired ceramic is somewhat independent of the starting particle size of the powder; however, there

is an apparent correlation with the tantalum oxide content. This relationship is plotted in Figures 1 (a) and (b), where the results for the different starting sizes are grouped on the same curve.

Based on a simple geometric model of the ceramic microstructure, it is instructive to calculate the area concentration of grain growth inhibitor present, if we assume that the inhibitor accumulates as a distinct phase confined to the inter-grain region of the densified body. For the case of a cubically-close packed grain structure with uniformly thin grain boundaries (which is easy to calculate), if the size distribution is homogeneous, then the total number of unit cells is of the order of

$$\left[\frac{L}{a} \right]^3 \quad \text{per grain,}$$

where L = length of the grain edge
 a = length of the unit cell edge, the unit cell being assumed cubic.

Also, the total number of unit cells which are adjacent to a grain boundary is about

$$6 \left[\frac{L}{a} \right]^2 \quad \text{per grain,}$$

so that the concentration of the latter type of unit cell ("interfacial" unit cell) is

$$\frac{6 \left[\frac{L}{a} \right]^2}{\left[\frac{L}{a} \right]^3} = \frac{6a}{L} \quad \text{mole fraction or} \\ \frac{600a}{L} \quad \text{mole percent.}$$

For a barium titanate the value of a is approximately $4 \text{ \AA}$; for a grain size of 1μ , i.e. $L = 1\mu$ or $10,000 \text{ \AA}$, the concentration of "interfacial" unit cells is therefore of the order of $1/4$ mole percent.

If we assume any other type of grain geometry with a homogeneous size distribution, for example a grain structure with a hexagonal cross section, it is evident that the value just quoted will not change by more than a factor of, say 2.

Examining Figure 1 (a) will give us the experimental value for the concentration of Ta_2O_5 required to sustain an average grain size of 1 micron, as about 1/2 weight percent, or 1/4 mole percent. This leads to the somewhat astonishing result that the total inhibitor concentration is of the order of one molecular unit per pair of "interfacial" barium titanate unit cells; in other words, the concentration of grain boundary stabilizer is stoichiometrically equivalent to an inter-grain layer roughly monomolecular in thickness.

It should be pointed out that the values of grain size quoted in Figure 1 result from a 20 minute firing schedule. However, extending the schedule to several hours was found to produce negligible additional grain growth, so that the tantalum oxide constitutes a "stabilizer" in the rather strict sense.

This geometric model of the stabilized ceramic microstructure, with the additional assumption of a uniform area distribution of inhibitor, implies that the concentration of inhibitor is inversely proportioned to the average final grain size. Significantly, the data of Figure 1 and Table II follow this relationship within their experimental accuracy. In Figure 1 (b), the reciprocal average grain size is plotted against tantalum oxide content to give a straight line.

In summary, the use of 2.5 weight percent of Ta_2O_5 was found to inhibit grain growth to a final size of 0.2 microns, using sufficiently finely and homogeneously sized pure barium titanate starting materials, and a small amount of SiO_2 as a sintering aid. It is expected that the use of higher concentrations of Ta_2O_5 will result in proportionately smaller grain sizes.

Electron micrographs of polished and etched samples are reproduced in Figure 2. The specimens were replicated with polyvinyl alcohol, and shadowed with



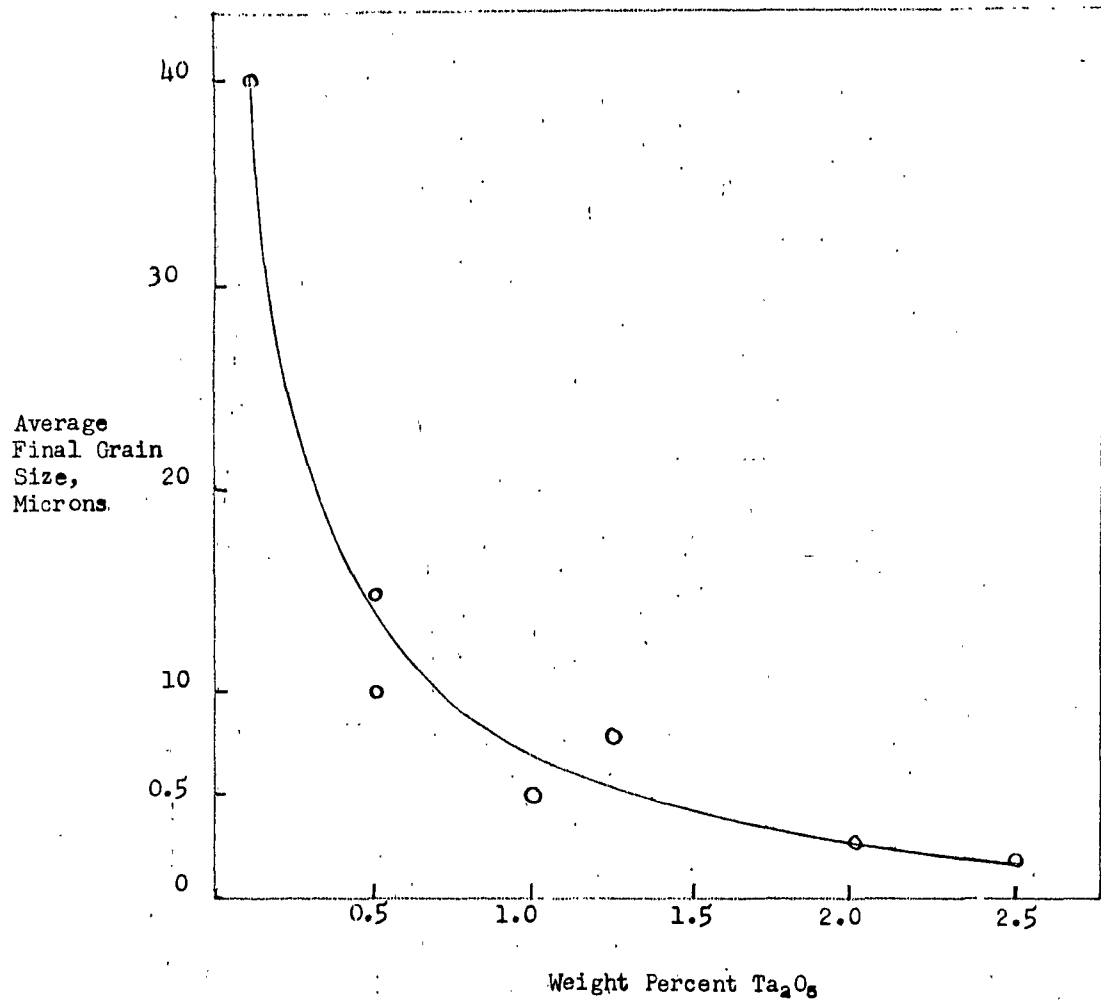


Figure 1a Effect of Ta_2O_5 content on grain growth of $BaTiO_3$ ceramic.



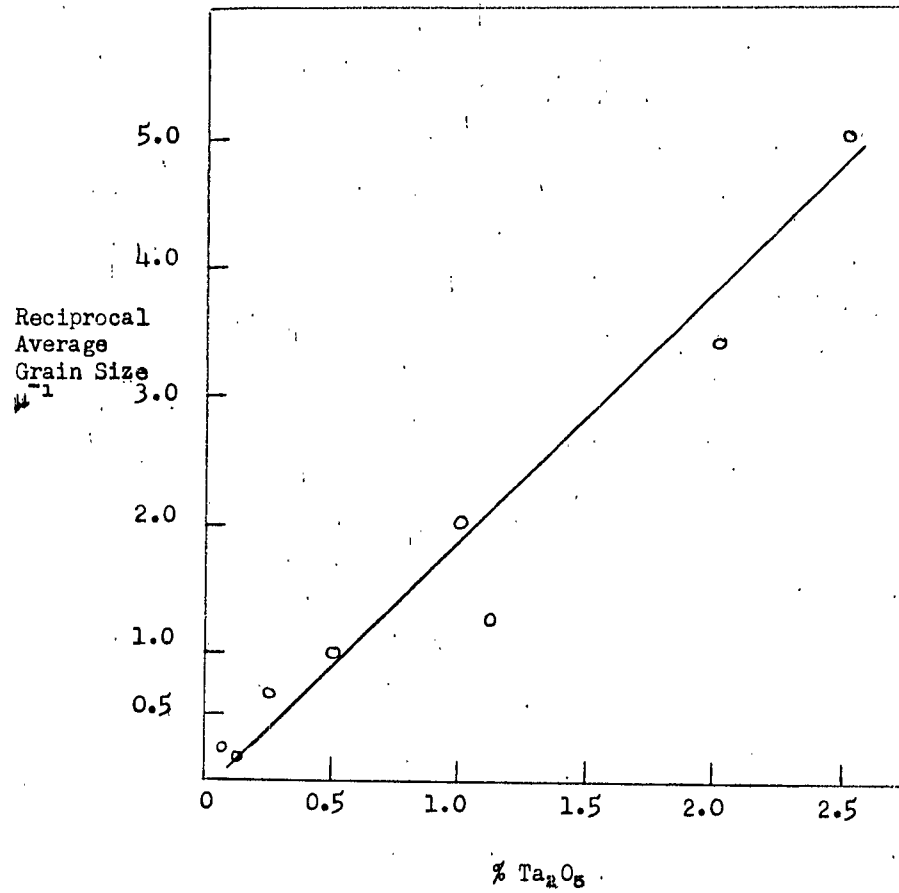
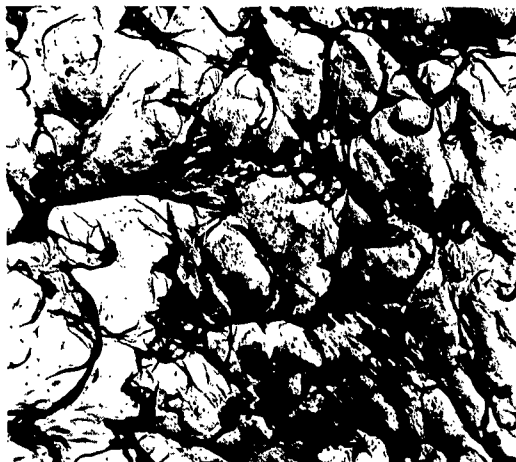


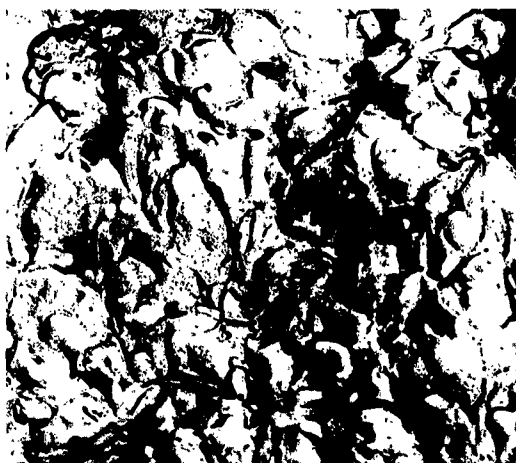
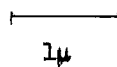
Figure 1b: Effect of Ta_2O_5 Content on Grain Growth of $BaTiO_3$ Ceramic.



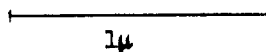
Figure 2: Electron micrographs of Ceramic BaTiO_3 with Ta_2O_5 added. Surfaces polished and etched.



10 micron grains



0.2 micron grains



platinum at 15° on a carbon backing. Due to porosity in the grain boundary region, it was difficult to replicate this area with perfect fidelity because of excessive local adhesion of the plastic film; however, the grain structure is unambiguously detailed.

1.3 Electrical Properties of Barium Titanate Ceramics with Controlled Grain Growth.

Graphs of dielectric constant and dissipation factor are plotted in Figures 3 and 4, for the bodies with grain sizes of 1.0 and 0.2 microns, respectively. The duplicate curves shown indicate the reproducibility of different specimens of the same composition and firing.

The larger grain size material shows a Curie peak at about 125°; however, it is extremely flat, representing an increase in dielectric constant K of only 5% over the room temperature. The lower temperature peak, corresponding to the tetragonal-or orthorhombic phase change in the vicinity of 0°, is absent from this body. Compare this to the curve in Figure 5, which represents the behavior of a control material of identical composition, except with no Ta₂O₅ added, and grain sizes averaging about 40 microns.

The electrical properties of the body inhibited to 0.2 micron grains show even more marked differences. In Figure 4, the Curie point has disappeared entirely from the temperature range measured, -40° to 180°C. In fact, K shows an extremely smooth variation from about 2800 to 750 as the temperature is increased.

Figures 6, 7, and 8 show the hysteresis loops for the samples corresponding to Figures 3, 4, and 5, respectively. The finest grain sized body exhibits a marked reduction in the area of the loop; the material is not appreciably ferroelectric until the application of higher fields. The behavior of the 1.0 micron body is intermediate between the larger and smaller grain size behavior.

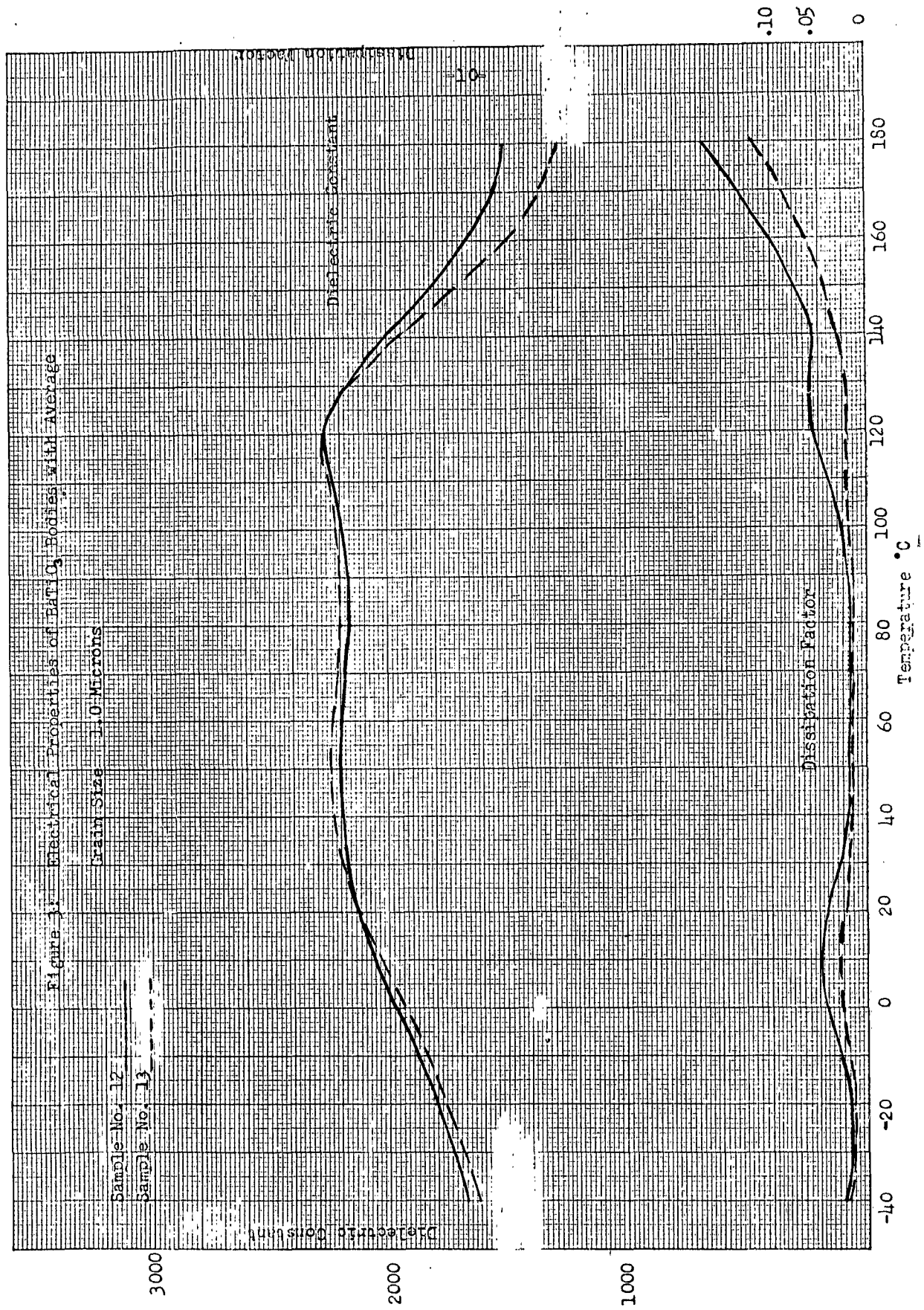


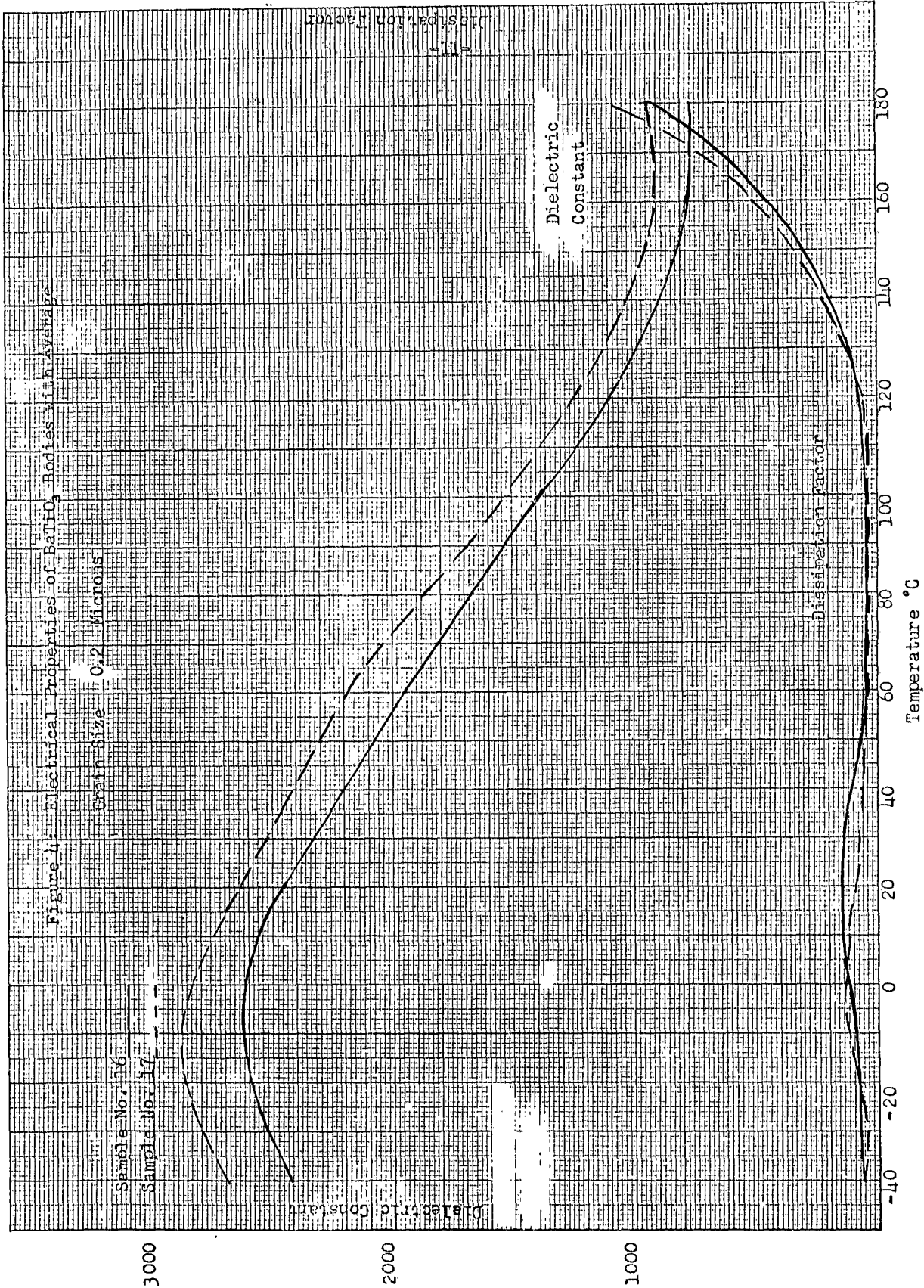
Figure 3. Electrical Properties of B10₃ Bores with Average

Grain Size 1.0 Microns

Sample-No. 12

Sample No.	13
------------	----





0
.05
.10

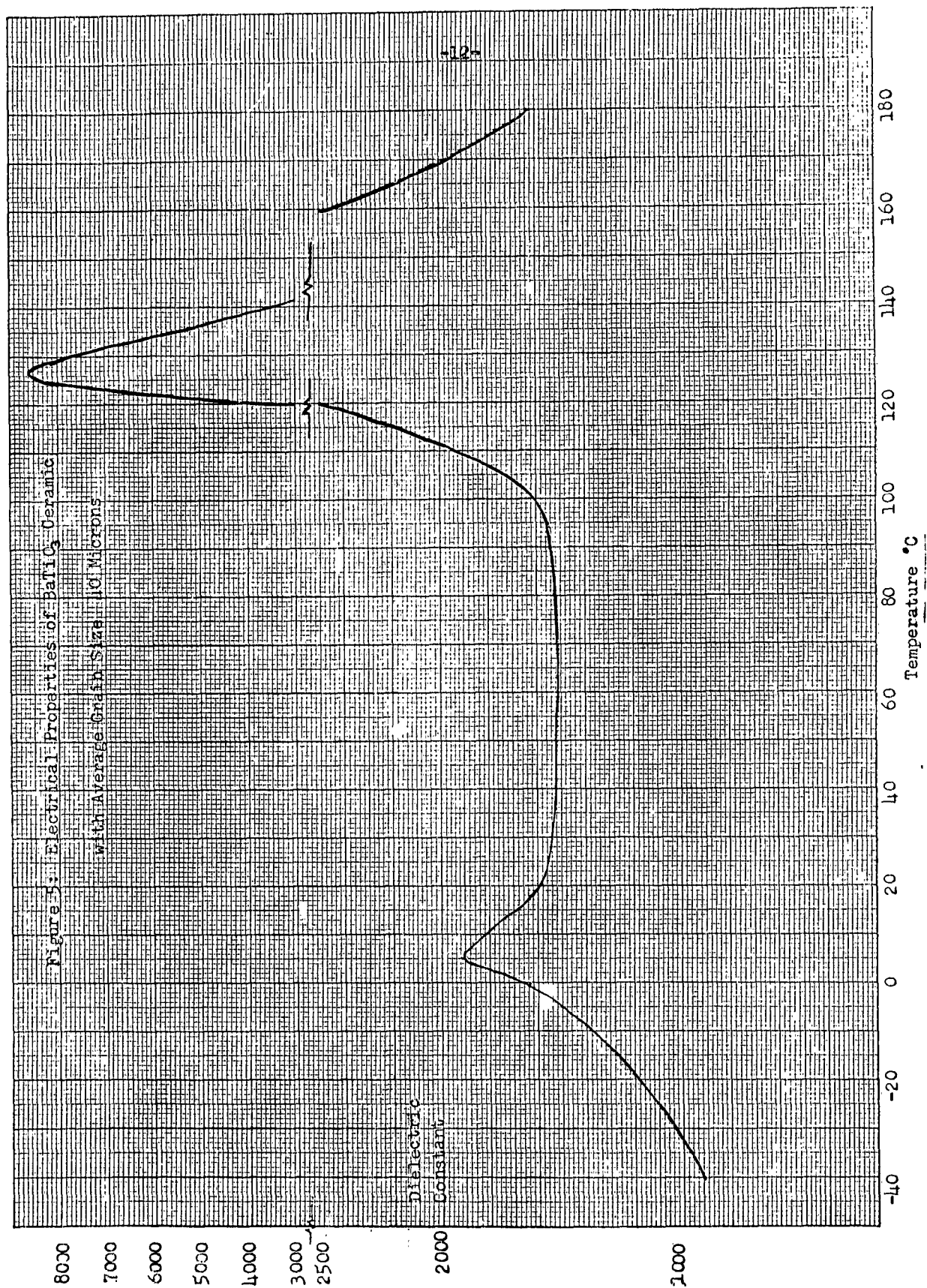
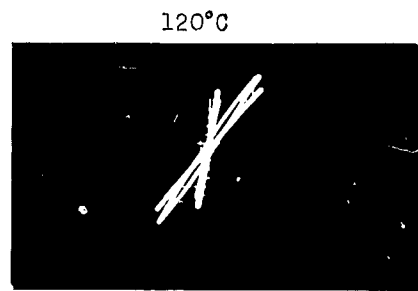
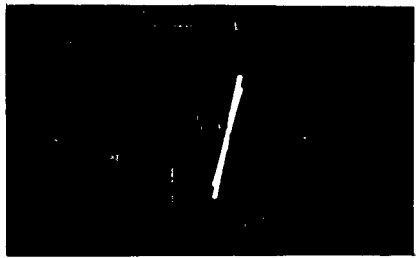
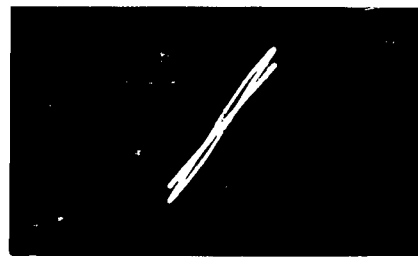
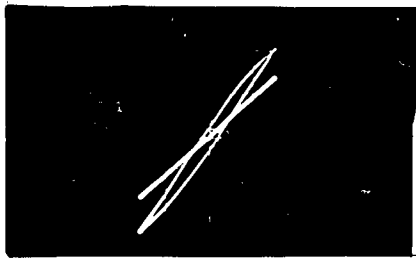


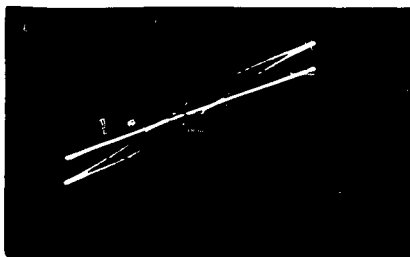
Figure 6: Hysteresis loops of BaTiO_3 Bodies with average grain size 1.0μ .
See figure 8 for legend.
25°C



1.7 kV/cm



8.3 kV/cm



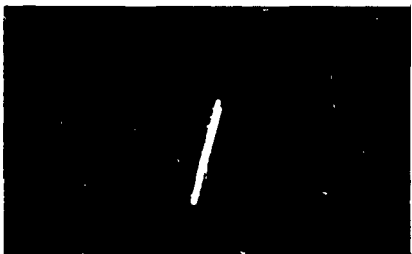
17 kV/cm



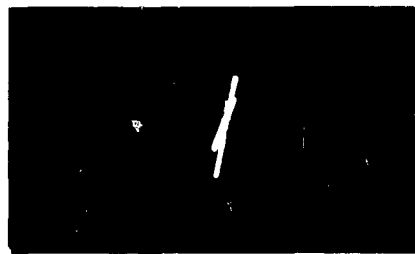
25 kV/cm

Figure 7: Hysteresis loops of BaTiO_3 bodies with average grain size 0.2μ .
See figure 8 for legend.

25°C



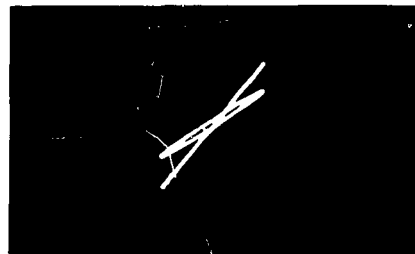
120°C



1.7 kV/cm.



8.3 kV/cm.



17 kV/cm.

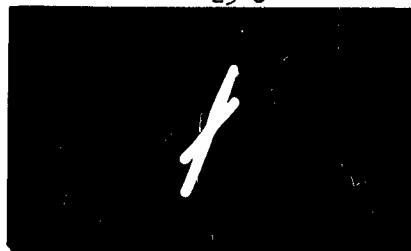


25 kV/cm.

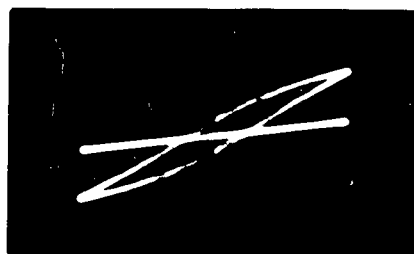
Figure 8: Hysteresis Loops of BaTiO_3 bodies
with average grain size,
 40μ , 25°C

Curves at corresponding field strengths
in Figures 6, 7, and 8, are plotted to
the same scales of field strength and
polarization, for purpose of
comparison.

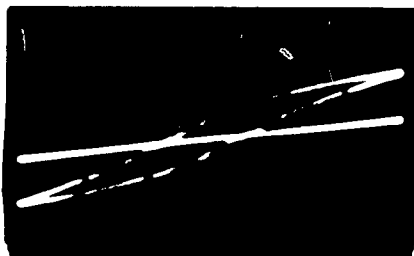
25°C



1.7 kV/cm.



8.2 kV/cm.



17 kV/cm.



25 kV/cm

The dielectric breakdown fields are as follows. Values listed are averages of duplicates, and sample thickness was about 0.06 cm.

TABLE III

Breakdown Fields of Inhibited Grain Size BaTiO₃ Ceramics

<u>Average Grain Size</u>	<u>% Ta₂O₅</u>	<u>Breakdown Field kV/cm.</u>
1.0	0.5	68.
0.2	2.5	60.
40.	0	52.

The addition of Ta₂O₅ and consequent reduction in grain size appears to have improved the breakdown field to some extent.



2. MIXED TITANATES IN ULTRA-FINE PARTICLE SIZES DERIVED FROM THE PYROLYSIS OF THE OXALATES.

2.1 Background

On account of the ease with which controlled fine particle size barium titanate powders of high purity may be obtained by the pyrolysis of barium titanyl oxalate, a certain amount of effort was directed to the preparation of mixed calcium barium titanate using analogous reactions. The reason for this selection is two-fold. First of all, our experiments indicated that the smallest particle sizes of barium titanate obtainable by a direct pyrolysis reaction are not smaller than about 500A°, but sizes as small as 100A° were desired. Theoretical considerations relative to the mechanism of the pyrolysis reaction suggested that if it were possible to prepare a mixed calcium barium titanyl oxalate, say, then its thermal decomposition might result in particles appreciably smaller than 500A°.

Secondly, the substitutional introduction of calcium into the barium titanate lattice results in a solid solution with a higher Curie point and a reduced temperature variation of dielectric constant (2),(3).

2.2 Experimental Methods

The methods reported generally in the literature for the synthesis of pure barium titanyl oxalate (4), (5) were not considered to be readily adaptable to the production of mixed alkaline earth titanyl oxalates. Accordingly, a new preparative method was developed, based on the decomposition of barium titanate by hot, concentrated solutions of oxalic acid.

In a typical experiment, 0.1 moles of C. P. grade barium titanate was dispersed in a 10% equivalent excess of a 50% solution of oxalic acid. Refluxing the mixture for a few minutes resulted in a precipitate of barium oxalate, and a solution of titanium oxalate. When the mixture was allowed to digest for 2 hours at 80°C, the



solid was converted to barium titanyl oxalate, and then removed by filtration in a substantially quantitative yield. The excess of oxalic acid was employed to retain in solution heavy metal and other impurities which readily form soluble oxalato complexes, thus improving the purity of barium titanyl oxalate.

Pyrolysis of the product at 1500°F for two hours resulted in barium titanate of a particle size identical to that derived from the similar treatment of a commercially obtained barium titanyl oxalate, averaging about 800 - 1000Å°. The procedure employed here was identical to that described in the last quarterly report of this contract.

For the production of fine particle mixed calcium barium titanate, a coarse particle material was first prepared, as follows. The desired molar ratios of C. P. grades calcium and barium titanates were blended, pressed into slugs, and calcined several hours at 2200°F. They were then disintegrated with a mortar and pestle, repressed and re-calcined. The disintegrated powder was then converted to the oxalate, identically to the pure barium titanate described above.

Pyrolysis of the product for 2 hours at 1500°F resulted in the mixed titanate.

Two base compositions have been prepared by this procedure; $\text{Ca}_{0.10}\text{Ba}_{0.90}\text{TiO}_3$, and $\text{Ca}_{0.03}\text{Ba}_{0.97}\text{TiO}_3$. The particle sizes of the 10 mole percent calcium material obtained by pyrolysis at 1500°F ranged closely about 150Å°, when the product was deflocculated with a 10% ammonium oleate solution.

The stoichiometry of the fine particled calcium barium titanate solid solution was established as follows. The compositions of coarse-particled solid solutions, prepared by the repeated calcination procedure, was calculated from the wet analyses of the pure calcium and barium titanate starting materials, since none of



the components are volatile under the reaction conditions employed. These coarse-particled materials were then used as calibration standards to obtain x-ray fluorescence intensity ratios for the BaO/TiO_2 and CaO/TiO_2 mole ratios. Then the corresponding mole ratios for the fine-particled solid solutions, derived from pyrolysis of the mixed oxalate, were calculated from their measured fluorescence intensity ratio. The exact technique is detailed in the second quarterly report of this contract.

It was found that the fine-particled material generally suffered a slight depletion of titanium, of the order of two or three percent, with the CaO/BaO ratio remaining virtually unaltered. This is no doubt due to the residual solubility of titanium oxalate in the supernatant liquid after the digestion step with oxalic acid. However, it should be possible to eliminate the titanium deficiency by reducing the amount of solvent present during the digestion step, or by adding, say, alcohol to reduce the solubility of titanium oxalate.

It should be pointed out that the current work on the synthesis of mixed calcium barium titanates is not part of a program for composition development. Rather, it has been introduced to add an extra degree of freedom to facilitate modifications of the barium titanate base material with regard to the bulk Curie point, and the ready accessibility of fine particles as small as $100\text{\AA}$.



3. ULTRA-FINE BaTiO₃ BY THE PRECIPITATION TECHNIQUE.

3.1 Objectives

The objectives of the studies performed during this period of the contract were to establish the reproducibility of the preliminary experiments to produce controlled size ultra-fine barium titanate, particularly when the syntheses were scaled up to 25-50 gram batches.

A study was also made of the effect of the recovery process, as defined below, on the BaO/TiO₂ ratio of the product, particularly since this ratio has been somewhat difficult to pre-determine in the preliminary experiments.

The processes by which BaTiO₃ of BaO/TiO₂ ratio 1.02 to 1.05 have been obtained utilizing chelated and non-chelated isopropyltitanate, respectively, have been described in the previous quarterly report of this contract. Particle sizes of the products were 100A° - 200A°, respectively.

3.2 Reproducibility Experiments

Table IV lists the results of particle size and stoichiometry measurements on duplicated batches of precipitated BaTiO₃, in two desired size ranges, (a) and (b). Reproduction of these properties has been successful.

TABLE IV

Reproducibility of Controlled Size BaTiO₃ by the Precipitation Technique.

(a) 100 - 200A°

<u>Sample No.</u>	<u>BaO/TiO₂ Ratio</u>	<u>Particle Size, A°</u>
13	1.019	100-200
18	1.065	80-250
22	1.058	100-200

(b) 400 - 1000A°

<u>Sample No.</u>	<u>BaO/TiO₂ Ratio</u>	<u>Particle Size, A°</u>
6	1.05	400-1000
29	1.08	600-1200



3.3 Effect of the Recovery Process on the BaO/TiO₂ Ratio

A study of the effect of the recovery process on the BaO/TiO₂ ratio was carried out on systems utilizing the hydrolysis of the chelated isopropyltitanate in a 1:1 water-isopropyl alcohol solution of Ba (OH)₂. The results of these experiments are summarized in Table V.

It was established by the comparison of experiments in which the conditions of the precipitation were identical, but the recovery process was varied, that the recovery process has a major effect on the BaO/TiO₂ ratio. Centrifugation of both the hot and cold slurry resulted in a lower BaO/TiO₂ ratio (0.841 and 0.95, respectively). The latter result being very close to unity, a reconsideration of the effect of cold centrifugation process is planned.

The BaO/TiO₂ ratio decreased drastically when the undried precipitate was digested with 0.2% formic acid (0.861) or when the precipitate was dried at a low temperature (116°C) for only one hour previous to the digestion (0.848).

The following recovery process seems to be the most favorable. After precipitation, the slurry is cooled to room temperature, stored for one to two hours, and is filtered through a fritted glass filter. The precipitate is washed with cold degassed distilled water two to three times. The weight of each quantity of wash water is about 40 times that of the weight of the precipitate. Finally the precipitate is dried in a vacuum oven at 120°C or higher.

Filtration of the precipitate becomes extremely slow when the particle sizes approach 100A°, therefore, it is preferable to carry out the filtration in an N₂ atmosphere to prevent BaCO₃ formation during the lengthy filtering step.

Due to the disadvantage of filtering slowly, further experiments are necessary to review separation by centrifuging and other possible recovery methods are to be



TABLE V

Sample No.	Method of Separation	Temperature of Separation	Effect of the Recovery Process on the BaO/TiO ₂ Ratio		Digestion with 0.2% Formic Acid	Ba/Ti Ratio
			Cold Water Wash	Treatment of Precipitate Before Digestion		
271	Filtration	Cold	Not Used	---	---	1.15
18	Filtration	Cold	Used	---	---	1.065
22	Filtration	Cold	Used	Dried at 190°C for 5 hours	200cc for 4 g precipitate	1.058
13	Filtration	Cold	Used	Dried at 190°C for 3 hours	"	1.019
25	Filtration	Cold	Not Used	Dried at 190° for 4 hours	1000cc for 4 g precipitate	0.99
192	Filtration	Hot	Used	---	---	0.944
20	Centrifugation	Cold	Used	---	---	0.95
191	Centrifugation	Hot	Used	---	---	0.841
161	Filtration	Cold	Used	Undried	200cc for 4 g Precipitate	0.861
162	Filtration	Cold		Dried at 1160C For 1 hour	"	0.848

assessed to suit the production of larger quantities.

3.4 Scaling Up

BaTiO₃ of BaO/TiO₂ ratio = 1.08 was obtained by the hydrolysis of isopropyltitanate in a water solution of Ba(OH)₂ in a batch increased by a factor of 5 compared to a former experiment. The particle size of the product was 600-1200Å*, very close to the predicted 400-1000Å*.

The experimental work indicated two major problems: difficulties in the filtration step, and an increase in the BaO/TiO₂ ratio.

3.5 Densification of Ultra-Fine BaTiO₃

Various attempts were made to densify bodies from the materials in the two particle size ranges (a) and (b) listed in Table III, using flash and extended firing cycles, without the incorporation of any additives. However, the resulting bodies could not be densified to greater than about 80%.

This difficulty is ascribed to both the high purity and extremely fine particle size of the material. When a sample of the powder is heated in a flame, it exhibits a "recalescence" phenomenon, i.e. the sudden liberation of heat accompanying a rapid decrease in the surface area at temperatures several hundred degrees below the bulk fusion temperature. For materials of extremely high surface area, i.e. high surface energy, it is possible that the heat liberated is sufficient to induce local fusion. Small pellets of the material sintered as low as 2300°F exhibit non-porous surfaces but porous interiors, when examined in section under the microscope. This suggests that the surface of the particle fuses prematurely.

An approach to increasing the densification of this material is the use of a very slow heating cycle, or the addition of high concentrations of grain growth inhibitors.



4. PRECIPITATION OF BaTiO_3 FILMS FROM HOMOGENEOUS SOLUTION

In view of the successes which had been experienced in this laboratory in obtaining barium titanate of a reproducible particulate character, by the use of soluble barium and organic titanium compounds, preliminary experiments were directed to the precipitation of films of barium titanate directly from homogeneous solution. The objective was to obtain a coherent polycrystalline film of barium titanate with a sub-optical crystallite size. By subjecting such a material to controlled heat treatments, a full range of larger grain sizes might be obtainable.

One particular system was selected by virtue of the particular reactivity of the starting materials, which facilitated manipulation without fear of premature deposition of barium titanate, or of reaction times too slow to be practical. This system comprised the reaction between barium acetate, and an equivalent amount of a titanyl acylate in a glacial acetic acid medium. When the reactants were mixed in suitable proportions, a precipitate formed after a period of several hours at room temperature, and more rapidly at elevated temperatures. When dried and calcined at 1000°F , the reaction product was identified, by x-ray diffraction and x-ray fluorescence, as stoichiometric barium titanate.

In a typical experiment, 10.5 g. of barium acetate was dissolved in 20 g. of boiling glacial acetic acid, and cooled to 25°C . It was then mixed with 13.6 g. of tetrabutyltitanate, and evacuated with stirring while warming to 50° over a period of 3 hours, in order to complete the reaction of the titanate ester to form the butoxy titanyl acetate, by the volatilization of part of the butyl alcohol (6). The resulting product was a clear orange viscous solution, containing the equivalent of about 21% BaTiO_3 .

A few drops of the material were spread on a glass plate, which was then



placed in a covered dish to inhibit evaporation, since the lower molecular weight titanate acylates (i.e. the unpolymerized species) are not entirely involatile. In about 12 hours, a gel had formed, which on subsequent evaporation, had cracked so as to lose its coherency.

To date, the use of various dilutions by acetic acid has not been successful in preventing gel formation, so that coherent films of barium titanate have not been obtained. However, it is possible that the introduction of higher boiling solvents of appropriate polarity into the reaction system may sustain the fluidity of the solution during the solvent evaporation process. Such additives which might be suitable are glycol monoethers, which have been found to be miscible with the reaction system.



PROGRAM FOR THE NEXT CONTRACT PERIOD

During the next period of this project, films will be prepared in a range of thicknesses by deposition from dispersions of high purity fine particle barium titanate, with particles coated with small quantities of SiO_2 , and Ta_2O_5 to control the grain size of the fired film. For these preparations, white room facilities will be used to ensure freedom from dust contamination.

The films will be electroded and characterized electrically, the properties to be determined as a function of grain size.

Other formulations based on fine homodisperse calcium barium titanate materials, obtained by the method of pyrolysis of the oxalate, will also be studied, since these solid solutions may offer improvements in the desired electrical requirements, based on their elevated Curie points.

A further study will be made of the feasibility of depositing barium titanate from reactions in homogeneous solution, by attempting to restrict the formation of intermediate gel phases.

Efforts will be directed to overcoming the deleterious effects of the rapid release of energy when ultra-fine particles, obtained by the precipitation technique, are sintered, by using slow programmed heating cycles.



References

1. D. E. Rase and Rustum Roy, J. AM. Ceram. Soc. 38 (11), 393 (1955)
2. Wright Air Development Center Contract No. AF 33 (616) - 3041,
"Ferroelectric Devices", Technical Report 56-362
ASTIA Document No. AD97124 (December, 1956)
3. Wright Air Development Center Contract No. AF 33 (600) - 31966,
"Ceramic Capacitors with Wide Temperature Range for
Printed Circuits".
4. J. Res. National Bureau of Standard, 56 289-91 (1956)
Res. Paper No. 2677.
5. U. S. 2,827,360, W. Blumenthal, March 18, 1958, to
National Lead.
6. U. S. 2,621,195, J. H. Haslam, December 9, 1952, to
E. I. du Pont.



Identification of Personnel

Eugene Wainer
Eugene Wainer
Director of Research

Mark S. Vukasovich
Mark S. Vukasovich
Head, Ceramics Department

Jules Magder
Jules Magder
Project Supervisor

Richard A. Fotland
Richard A. Fotland
Head, Physics Department

Klara Kiss
Klara Kiss
Research Associate

Theodore M. Harkulich
Theodore M. Harkulich
Research Associate



UNITED STATES ARMY SIGNAL RESEARCH AND DEVELOPMENT LABORATORY
STANDARD DISTRIBUTION LIST
RESEARCH AND DEVELOPMENT CONTRACT REPORTS

Copies

- 1 Technical Library, OASD (R and E), Room 3E1065
The Pentagon, Washington 25, D. C.
- 1 Chief of Research and Development, OCS,
Department of the Army, Washington 25, D. C.
- 1 Commanding General, U. S. Army Material Command
Attn: R and D Directorate, Washington 25, D. C.
- 1 Commanding General, U. S. Army Electronics Command
Attn: AMSEL-AD, Fort Monmouth, New Jersey
- 1 Director, U. S. Naval Research Laboratory
Attn: Code 2027, Washington 25, D. C.
- 1 Commander, Aeronautical Systems Division,
Attn: ASAPRL, Wright-Patterson Air Force Base, Ohio
- 1 Headquarters, Electronic Systems Division, Attn: ESAL
E. G. Hanscom Field, Bedford, Massachusetts
- 1 Commander, Air Force Cambridge Research Laboratories
Attn: CRO, L. G. Hanscom Field, Bedford, Massachusetts
- 1 Commander, Air Force Command and Control Development Division
Attn: CRZC, L. G. Hanscom Field, Bedford, Massachusetts
- 1 Commander, Rome Air Development Center, Attn: RAALD
Griffiss Air Force Base, New York
- 1 Deputy President, U. S. Army Security Agency Board
Arlington Hall Station, Arlington 12, Virginia
- 10 Commander, Armed Services Technical Information Agency
Attn: TISIA, Arlington Hall Station, Arlington 12, Virginia
- 2 Chief, U. S. Army Security Agency,
Arlington Hall Station, Arlington 12, Virginia
- 1 Commanding Officer, Harry Diamond Laboratories
Attn: Library, Room 211, Building 92, Washington 25, D. C.
- 1 Corps of Engineers Liaison Office, U. S. Army Electronics Research
and Development Laboratory, Fort Monmouth, New Jersey

Standard Distribution List (cont'd).

Copies

- 1 AFSC Scientific/Technical Liaison Office
U. S. Naval Air Development Center, Johnsville, Pennsylvania
- 1 Commanding Officer, U. S. Army Electronics Material Support Agency
Attn: SELMS-ADJ, Fort Monmouth, New Jersey
- 1 Marine Corps Liaison Office, U. S. Army Electronics Research and
Development Laboratory, Attn: SELRA/LNR, Fort Monmouth, New Jersey
- 1 Commanding Officer, U. S. Army Electronics Research and Development
Laboratory, Attn: Director of Research or Engineering, Fort Monmouth,
New Jersey
- 1 Commanding Officer, U. S. Army Electronics Research and Development
Laboratory, Attn: Technical Documents Center, Fort Monmouth, New Jersey

Horizons Incorporated
DA36-039 sc-89203

SUPPLEMENTAL DISTRIBUTION LIST

Copies

- 1 Aeronautronic Incorporated, Division of Ford Motor Company
Attn: Dr. Lloyd P. Smith, Ford Road, Newport Beach, California
- 1 Aeroprojects Incorporated, Attn: Dr. Harold L. McKaig, Jr.
310 East Rosedale Avenue, West Chester, Pennsylvania
- 1 Carborundum Company, R and D Division, Attn: Dr. W. A. Lamberton
P. O. Box 337, Niagara Falls, New York
- 1 Cornell Aeronautic Laboratory, Incorporated, Materials Department,
Attn: Dr. Henry P. Kirchner, Buffalo 21, New York
- 1 Eastman Kodak Company, A and O Division, Camera Works
Attn: Mr. T. H. Robinson, 400 Plymouth Avenue, North, Rochester 4, New York
- 1 Electro Ceramics, Incorporated, Attn: Dr. Edmond P. Hyatt
2645 South Second, West, Salt Lake City 15, Utah
- 1 General Electric Company, Electronics Research Laboratory,
Attn: Dr. E. C. Henry, Building 23, Electronic Park, Syracuse, New York
- 1 General Instrument Corporation, Attn: Dr. Manfred Mannheimer
65 Couverneur Street, Newark, New Jersey
- 1 General Telephone and Electronics Laboratories, Incorporated,
Bayside Laboratories, Attn: Dr. A. L. Solomon, Bayside 60, New York
- 1 Gulton Industries, Incorporated, Attn: Mr. Norman Rudnick
212 Durham Avenue, Metuchen, New Jersey
- 1 Ionics Incorporated, Attn: Dr. Carl Berger, 152 Sixth Street
Cambridge, Massachusetts
- 1 Federal Telecommunication Laboratories, Division of International Telephone
and Telegraph Corporation, Attn: Dr. P. E. Lighty
500 Washington Avenue, Nutley 10, New Jersey
- 1 Materials Research Corporation, Research Division, Attn: Dr. Sheldon Weinig
47 Buena Vista Avenue, Yonkers, New York
- 1 Melpar Incorporated, A Subsidiary of Westinghouse Air Brake Company,
Attn: Dr. Joseph L. Pentecost, 300 Arlington Boulevard, Falls Church, Virginia
- 1 Solid State Materials Corporation, Attn: Dr. Joseph F. Wenkus
5 Erie Drive, Industrial Park, East Natick, Massachusetts

Supplemental Distribution List (cont'd)

Copies

- 1 Speer Carbon Company, Research Laboratory, Attn: Dr. F. M. Collins
Packard Road and 47th Street, Niagara Falls, New York
- 1 Stanford Research Institute, Attn: Dr. Frank A. Holden
Menlo Park, California
- 1 Sylvania Lighting Products, A Division of Sylvania Electric Products
Incorporated, Attn: Dr. Deith Butler, 60 Boston Street, Salem, Massachusetts
- 1 Tem-Press Research Incorporated, Attn: Dr. Bert Phillips
146 North Atherton Street, State College, Pennsylvania
- 1 Titanium Alloy Manufacturing Division, National Lead Company, Research
Laboratory, Attn: Dr. Stephen F. Urban, Niagara Falls, New York
- 1 Vitro Laboratories, West Orange Laboratory, Attn: Dr. Stanley Grande
200 Pleasant Valley, West Orange, New Jersey
- 1 Norden Division of United Aircraft Corporation, Chief Research and
Development, Norden Division, Attn: Mr. B. Tatom, Norwalk, Connecticut
- 1 Clevite Corporation, Electronic Research Division, Attn: Mr. Bernard Jaffe
P. O. Box 5089, Cleveland, Ohio
- 1 Linden Laboratories, Incorporated, Attn: Dr. W. R. Buessem and Paul A.
Marshall, State College, Pennsylvania
- 1 Houdry Processing, Incorporated, Attn: Dr. Joseph Donovan
P. O. Box 422, Marcus Hook, Pennsylvania
- 1 E. I. DuPont de Nemours and Company, Attn: Dr. G. J. Carignan
Wilmington 98, Delaware
- 1 Astron Corporation, Attn: John C. Froemel
255 Grant Avenue, East Newark, New Jersey
- 1 Hi-Q Division, Aerovox Corporation, Attn: Dr. A. Rodriguez
Olean, New York
- 1 Corning Glass Works, Attn: Dr. T. C. MacAvoy
Corning, New York
- 1 Sprague Electric Company, Attn: Mr. J. Bafricuis
North Adams, Massachusetts
- 1 Erie Technical Ceramics, Division of Erie Resistor Corporation
Attn: Mr. L. Kopeill, State College, Pennsylvania
- 1 Raytheon Company, Research Division,
Attn: Dr. Peter Nutter, Seyon St., Waltham, Massachusetts



Supplemental Distribution List (cont d)

Copies

- 1 N. J. Ceramic Research Station, Rutgers, The State University,
Attn: Prof. E. J. Smoke, New Brunswick, New Jersey
- 1 Aeronautical Systems Division, Attn: ASRCP-Mr. J. Wittebort,
Wright-Patterson Air Force Base, Ohio
- 1 Monsanto Chemical Company, Development Department, Research and Engineering
Division, Attn: Mr. Edward Orban, Lindburg and Olive Street Road,
St. Louis 24, Missouri
- 1 North Carolina State College, Department of Engineering Research
Attn: Dr. S. W. Derbyshire, Raleigh, North Carolina
- 1 Allen Bradley Corporation, Attn: Dr. G. Economos,
136 West Greenfield Ave., Milwaukee, Wisconsin
- 1 Philco Corporation, Attn: Mr. Robert Murphy
Blue Bell, Pennsylvania
- 1 National Science Foundation
Attn: Dr. Wayne Gruner, Washington 25, D. C.
- 1 Bell Telephone Laboratories, Metallurgical Division,
Attn: Dr. R. Rigterink, Murray Hill, New Jersey
- 1 Radio Corporation of America, Materials Semiconductor Division
Attn: Dr. B. Schwartz, Somerville, New Jersey
- 1 Metal and Thermit Corporation, Research Laboratory,
Ceramic Department, Rahway, New Jersey



AD	Accession No.	UNCLASSIFIED	AD	Accession No.	UNCLASSIFIED
Horizons Incorporated, Cleve. Ohio	ULTRA-FINE PARTICLE SIZE FERRO-ELECTRICS, J. Magder, K. Kiss	1. Barium Titanate 2. Ferroelectric Materials 3. Fine-particled Ferroelectric Materials	Horizons Incorporated, Cleve. Ohio	ULTRA-FINE PARTICLE SIZE FERRO-ELECTRICS, J. Magder, K. Kiss	1. Barium Titanate 2. Ferroelectric Materials 3. Fine-particled Ferroelectric Materials
Third Quarterly Progress Report, 16 October, 1962 to 15 January, 1963.	Signal Corps Contract DA36-039-sc-89203	Unclassified Report	Third Quarterly Progress Report, 16 October, 1962 to 15 January, 1963.	Signal Corps Contract DA36-039-sc-89203	Unclassified Report
Ceramic barium titanate of pre-determined, controllable grain size 2000A* average and larger were prepared, using tantalum oxalate and colloidal silica deposited on the surface of high purity powdered material before firing. Such bodies showed reduced temperature variations		(over)	Ceramic barium titanate of pre-determined, controllable grain size 2000A* average and larger were prepared, using tantalum oxalate and colloidal silica deposited on the surface of high purity powdered material before firing. Such bodies showed reduced temperature variations		(over)
AD	Accession No.	UNCLASSIFIED	AD	Accession No.	UNCLASSIFIED
Horizons Incorporated, Cleve. Ohio	ULTRA-FINE PARTICLE SIZE FERRO-ELECTRICS, J. Magder, K. Kiss	1. Barium Titanate 2. Ferroelectric Materials 3. Fine-particled Ferroelectric Materials	Horizons Incorporated, Cleve. Ohio	ULTRA-FINE PARTICLE SIZE FERRO-ELECTRICS, J. Magder, K. Kiss	1. Barium Titanate 2. Ferroelectric Materials 3. Fine-particled Ferroelectric Materials
Third Quarterly Progress Report, 16 October, 1962 to 15 January, 1963.	Signal Corps Contract DA36-039-sc-89203	Unclassified Report	Third Quarterly Progress Report, 16 October, 1962 to 15 January, 1963.	Signal Corps Contract DA36-039-sc-89203	Unclassified Report
Ceramic barium titanate of pre-determined, controllable grain size 2000A* average and larger were prepared, using tantalum oxalate and colloidal silica deposited on the surface of high purity powdered material before firing. Such bodies showed reduced temperature variations		(over)	Ceramic barium titanate of pre-determined, controllable grain size 2000A* average and larger were prepared, using tantalum oxalate and colloidal silica deposited on the surface of high purity powdered material before firing. Such bodies showed reduced temperature variations		(over)

of dielectric constant between -40° and $+180^{\circ}\text{C}$, and reduced Curie temperature peaks, when the grain sizes were less than about $5000\text{\AA}$.

Mixed calcium barium titanates of high purity were prepared by the pyrolysis of a mixed intermediate oxalate, produced by a novel technique.

of dielectric constant between -40° and $+180^{\circ}\text{C}$, and reduced Curie temperature peaks, when the grain sizes were less than about $5000\text{\AA}$.

Mixed calcium barium titanates of high purity were prepared by the pyrolysis of a mixed intermediate oxalate, produced by a novel technique.

of dielectric constant between -40° and $+180^{\circ}\text{C}$, and reduced Curie temperature peaks, when the grain sizes were less than about $5000\text{\AA}$.

Mixed calcium barium titanates of high purity were prepared by the pyrolysis of a mixed intermediate oxalate, produced by a novel technique.

of dielectric constant between -40° and $+180^{\circ}\text{C}$, and reduced Curie temperature peaks, when the grain sizes were less than about $5000\text{\AA}$.

Mixed calcium barium titanates of high purity were prepared by the pyrolysis of a mixed intermediate oxalate, produced by a novel technique.