1968 ELECTRONIC COMPONENTS CONFERENCE

May 8, 9, 10, 1968

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FOREWORD

A record number of abstracts were offered for presentation at the 1968 Electronic Components Conference. The Program Committee found that a large proportion of these were relevant and of sufficient interest and quality to qualify for acceptance. Every effort was made to include as many as possible on the program in order to provide our conferees with the broadest possible exposure to the latest scientific and engineering developments. Consequently, the sessions contain a greater number of papers on the average, than in previous years. More significantly, it was decided with some regret to do without the opening keynote speech on an experimental basis this year, a function which will now be supplied by the banquet address.

As usual, a large number of the papers presented deal with discrete components in improved or novel forms, which underlies their continuing importance in current and future circuit technology. However, the Electronic Components Conference has become a forum for discussion of many diverse technical activities related to the preparation and performance of electronic circuits in total. This is evident in the increasingly large number of papers given this year which are related in one way or another to hybrid integrated circuit technology. Moreover, a trend of last year continues in that interest is particularly strong in thick films. The schedule reflects this interest by including two sessions on this subject.

The related topics of packaging and interconnection continue in high interest. Of all the abstracts received 30% were in this area and it was with some difficulty that those accepted could be given in just two sessions.

A highlight of the 1968 program is the group of four excellent papers on different filtering techniques which forms a part of the session on Integrated Components and Filters. These four cover a broad range of frequencies and types of operation.

The emphasis on inductive elements this year has been on ferrite materials, and several papers of this type are involved. A strong involvement in materials as applied to all phases of circuit technology is evident throughout the entire program. This characteristic underscores the interdisciplinary nature of this meeting and provides a common basis for the many diverse elements making up this conference which have as their common objective the development of improved electronic circuitry.

The Program Committee has worked diligently to provide for the presentation of outstanding papers in the forefront of advancing technology. They hope the conferees will find much of interest and value.

<div style="text-align:right">

F. M. Collins
Technical Program Chairman

R. A. Gerhold
General Chairman

</div>

Banquet Address—Dr. Thomas O. Paine
    Deputy Administrator, National Aeronautics and Space Administration
    "Underdeveloped America—The Social Software Problem."

Panel Discussions
    "Ceramic Substrates"
    Moderated by David L. Wilcox, IBM

    "Computerized Design of Art Work and Documentation"
    Moderated by Arthur W. Sinkinson, RCA Aerospace Systems Division.

    "Micro-Miniature Interconnections"
    Moderated by Paul Mallery, Bell Telephone Laboratories.

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*Extended abstract—complete manuscript not available at time of publication.

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SESSION VII—Resistive Elements
Thursday p.m.
Chairman: D. Feldman

SESSION III—Materials
Wednesday p.m.
Chairman: M. A. Schwartz

SESSION IV—Thin Films
Wednesday p.m.
Chairman: P. D. Davidse

SESSION X—Interconnections
Friday a.m.
Chairman: R. J. Farquharson

SESSION VIII—Packaging
Thursday p.m.
Chairman: J. Staller

SESSION IX—Integrated Components and Filters
Friday a.m.
Chairman: A. Brodzinsky

A HIGH PURITY BARIUM TITANATE CAPACITOR

R. A. Piggott

Centralab Division of Globe Union Inc.
Milwaukee, Wisconsin

Summary. This paper compares the properties of high purity barium titanate (spectrographically pure) with those of the commerically pure materials relative to the formation of barium titanate barrier layer capacitors. The ability to make capacitors by reducing in different atmospheres has been investigated, using different electrode materials. Performance of high purity capacitors compared with commercial purity capacitors has been evaluated in terms of device characteristics such as: resistivity versus reduction temperature, temperature coefficient of resistance, capacitance, dissipation factor and leakage resistance. The properties of the unreduced ceramic material have been evaluated in terms of dielectric constant, grain size, porosity, temperature coefficient of capacitance. The effect of rawfiring temperature on grain growth has been studied relative to dielectric constant by metallography.

Key Words. (For Information Retrieval) -- Barium titanate, capacitors, high purity, polycrystalline, reduced, semiconducting.

Introduction

Some of the early work by researchers on barium titanate capacitors provided the ground work leading to today's technology. The theoretical treatment of the subject has, however, not been developed to such a great extent. Yield and reliability still give problems although high production capability methods have been developed. Failure analysis of barrier layer capacitors indicates that the physical properties of materials and their interrelationship must receive thoughtful consideration if high quality capacitor processes are to be attained. Most investigators have given considerable attention to dielectric constant, resistivity, loss tangent and other physical properties associated with capacitors. However, the ever mounting requirement for greater capacitance per unit area, higher capacitor operating voltage, and better temperature coefficient of capacitance has spurred research to obtain new materials and

new processes which may meet these needs. For these reasons it was felt that it may be fruitful to investigate the properties of a high purity barium titanate capacitor.

Buying Material From Outside Sources

Investigations of high purity barium titanate have normally been concerned with a very high purity barium titanate precipitated from the oxalate and has mainly been on a laboratory scale rather than in production quantities. This is due to the high cost of producing this very pure form of barium titanate.

For the present work, in view of the high cost of producing inhouse made barium titanate and its limited applicability to production quantity work, use was made of the less costly spectrographically pure barium titanate obtained from outside sources. This is intermediate in cost and its purity is between commercially pure material and very high purity inhouse made material. It was felt that capacitors made using this material may have better characteristics which would justify the higher cost.

Basis For Selection

As spectorgraphically pure barium titanate differs from vendor to vendor, samples of spectrographically pure barium titanate were obtained from several different vendors (22 vendors in all) and evaluated.

Since barium titanate is a dielectric in the normal state and becomes a semiconductor in the reduced state it is possible to evaluate the material as a dielectric or as a semiconductor. As a preparation for the work reported herein, the various basic ceramic materials were evaluated as a dielectric. This resulted in the selection of the two materials discussed in this paper. Both the dielectric and the semiconducting materials are utilized as capacitors depending on the characteristics of interest. As a semiconducting material is more likely to be affected by impurities than is a dielectric material it was of interest in the

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present work to study the case of a high purity barrier layer capacitor using semiconducting material. It was assumed that the dielectric properties of the barium titanate correlate with the device properties in the semiconducting state in view of the extensive work which would be required to evaluate all 22 ceramic materials in the semiconducting state.

It has been found subsequently that the device properties of the barrier layer capacitors were strongly dependant on the processing of the dielectric material. Two sets of process conditions were evaluated giving two lots of dielectric material designated lot 1 and lot 2. Commercial purity material was compared with the high purity material.

As the properties of lot 1 differ from the properties of lot 2, a brief description of the method of preparation of these materials follows.

Preparation of Material Lot 1

The material was moistened, milled and dried. The required amount of a wax emulsion was added as a binder. The material was mixed and screened and was then ready for pelleting.

Preparation of Material Lot 2

In this case the binder was made from a mixture of cellulose acetate and dibutyl phthalate. The binder was dissolved in acetone and added to the barium titanate and stirred. The barium titanate was then ready for pelleting.

Pelleting Conditions

The high purity material was pelleted by hand in a hydraulic toggle press to a green density of 56.5 g/in^3. Discs had a diameter of .636" and were 0.025inches thick. The commerically pure material was pelleted in an automatic press to a green density of 59.3 g/in^3. These densities are about 60% of the theoretical density (98.5 g/in^3).

Rawfiring

For high purity material lot 2, firings were carried out in a 4 inch tube kiln. The ceramic pushed into the furnace at 427°C. The furnace was then heated at approximately 232°C per hr. to the soak temperature. A flowing

atmosphere of 20% dry O_2 and 80% dry N_2 was maintained and a 1 hour soak period was used.

The high purity material lot 1 was rawfired at 1316°C for a 180 min. cycle. During firing discs were loaded with a refractory to reduce warpage. The commercially pure material was rawfired at 1299°C for a 24 hour cycle.

Data obtained for high purity material lot 2

Graphs of density and dielectric constant versus firing temperature were obtained as well as T.C. data for samples with fired density 88% of theoretical. The microstructure was examined.

Reduction

Specimens of each material were reduced in the gases, H_2, cracked NH_3 and forming gas (10%H_2, 90%N_2) at temperatures of 871°C, 927°C, 982°C, 1038°C, 1093°C, 1149°C respectively for a 2 hour soak period in a lab tube kiln.

Analysis of High Purity Materials

High purity materials used were designated as Comp "CA" and Comp "CB". Composition CA is manufactured by a major barium titanate source* and its composition is shown in Table I.

Comp. CB which is from a competitive source* was selected for composition similarity and its composition is shown in Table II.

Table I
Composition CA

Mat. wt.%	SrO	CaO	MgO	ZrO$_2$	Al$_2$O$_3$	SiO$_2$
	.08	.012	.052	.003	.005	.005

Mat. wt.%	Fe$_2$O$_3$	CuO	Na$_2$O	K$_2$O	P$_2$O$_5$
	.010	.002	.090	.070	.010

Mat. wt.%	SO$_3$	BaTiO$_3$
	.145	remainder

Particle size .2 - .4μm

* Composition "CA" was supplied by Titanium Manufacturing Division of the National Lead Co.

Composition "CB" was supplied by Transelco Inc.

Table II
Composition CB

Mat. wt.%	SrO .160	CaO .011	MgO .010	ZrO$_2$ .001	Al$_2$O$_3$ .002
Mat. wt.%	SiO$_2$ .070	Fe$_2$O$_3$ .015	CuO .003	Na$_2$O .020	K$_2$O .080
Mat. wt.%	P$_2$O$_5$ .170	SO$_3$ .015	BaTiO$_3$ remainder		

Particle size .50 - 2.00

These values are obtained from vendor stated characteristics and independant lab analysis.

The commercially pure materials contained Bi$_2$O$_3$ to act as a reduction catalyst and were designated as Comp. "CC" and Comp. "CD".

Barrier Layer Capacitor Design

Barrier layer capacitors,*using semiconducting barium titanate have been known for several years and since their discovery there has been a considerable effort put into improving their device characteristics. Normally commercially pure material is used preferably with additives, although high purity barium titanate has been shown by others to be useful.

Of importance in device design are:

1. T.C.
2. Voltage rating
3. Size and configuration (req'd. cap. density)
4. Dissipation

Voltage rating depends on IR. IR** and required capacity density are related to the reduction conditions in the following manner. As the reduction temperature is increased the resistivity of the material will decrease and consequently the leakage will decrease. It is found that under these circumstances the capacitance rises to a maximum after which it begins to decrease once again. The resistivity also decreases with increasing H$_2$ content of the reducing gas. These effects are shown in figures 1 and 2 below.

* U. S. Patent 2,841,508 Roup et al.

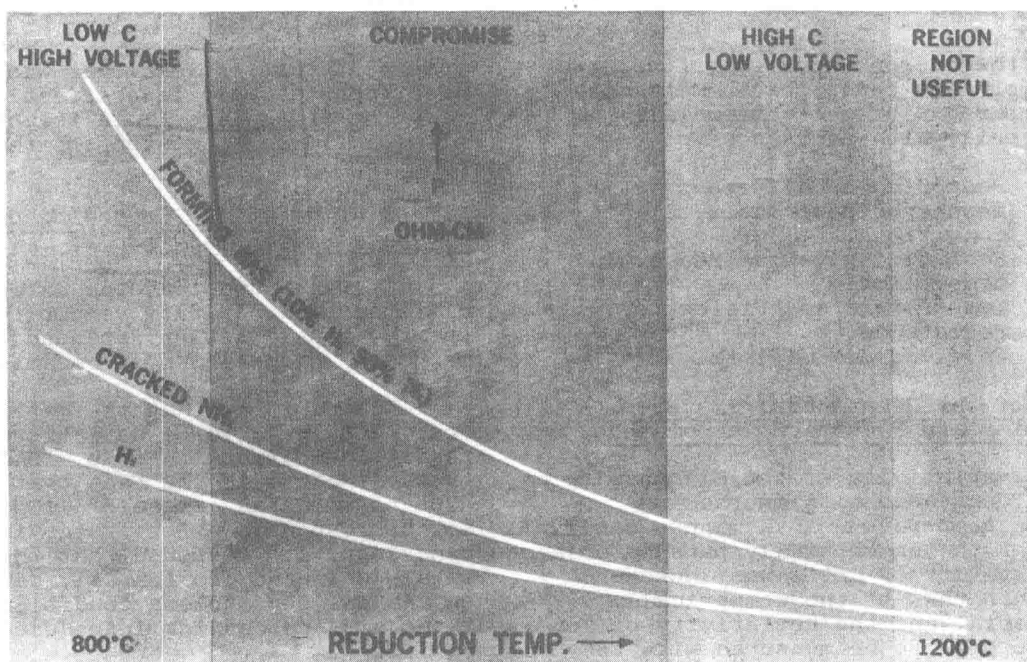** IR denotes insulation resistance or leakage resistance.

Fig. 1 Useful Resistivity Range for Device Design

| HIGH C LOW VOLTAGE | COMPROMISE | LOW C HIGH VOLTAGE | REGION NOT USEFUL |

C CURVE

IR CURVE

IR C

FIRING TIME (T) →

15 MIN.   35 MIN.
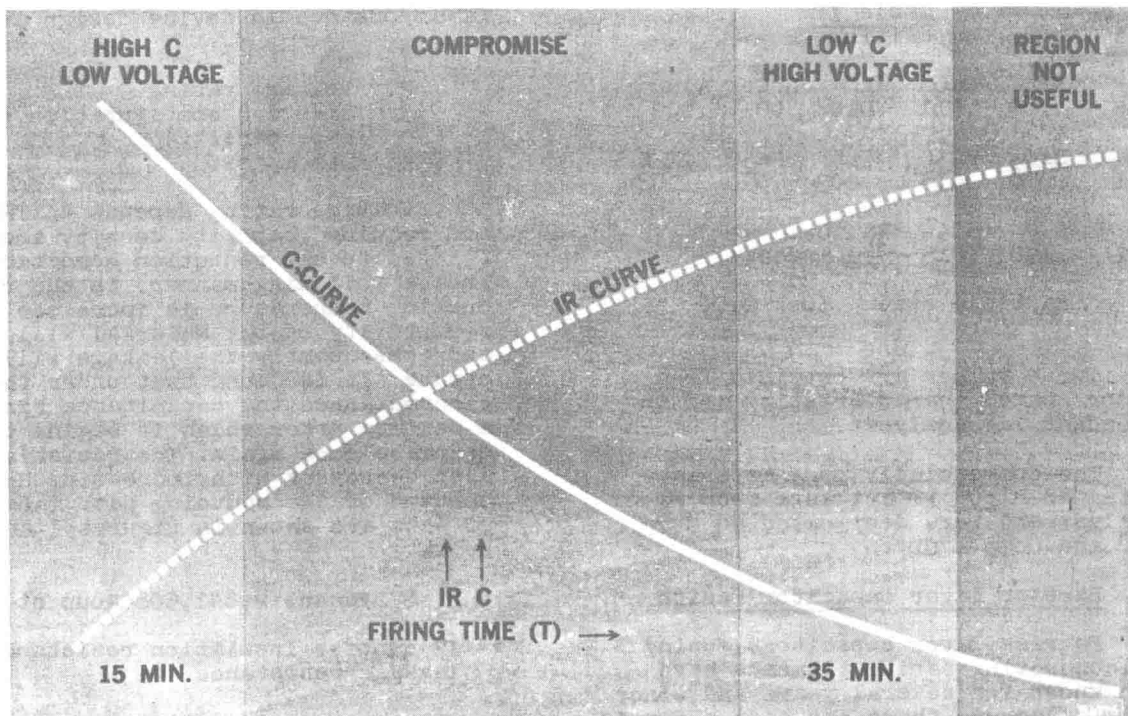
Fig. 2 Effect on Device Characteristics of Electrode Fire-On Time

$$C = \frac{KA}{t} \qquad C \propto \frac{1}{\rho}$$

$$IR = kt \qquad I.R. \propto \rho$$

In the present work therefore, two sources of high purity barium titanate were compared with the commercially pure material with reference to:

A. Reduction in different atmospheres under controlled conditions.
B. Resistivity versus reduction temperature.
C. Temperature coefficient of resistance.
D. An electrode material.

A Study of the Relationship Between Resistivity and Reduction Temperature

The resistivity of the high purity material decreased with increasing reduction temperature in a manner similar to that of the commercially pure material. The resistivity of lot 2 was, however, higher than that of the commerically pure material and the resistivity of lot 1 was two high to be measured with the 4 point probe.

Hydrogen and cracked NH_3 gave similar resistance vs reduction temp-

erature curves. Forming gas was, however, considerably less effective as a reducing atmosphere. This is consistent with the lower H_2 content of the forming gas.

Effect of Material Processing on Reduced Titanate Properties

It was found that the material differed not only from vendor to vendor but the final results depended on the method of preparation of ceramic discs.

It was found that the material comp. "CB" gave large deviations in the results compared with comp. "CA". A probable cause is the fact that comp. "CB" contains an excess of TiO_2 which may be responsible for its grainlike behaviour. It was found that the materials differed considerably depending on the milling process conditions. Some methods of processing introduce impurities.

Electrode Material Study

Three electrode materials were used

to observe the behaviour of high purity material. The compositions were designated as:

1. Composition "MA"
2. Composition "MB"
3. Composition "MC"

Composition MA is an unmodified purchased material used for paint formulations. Composition MB is the same base content but has a decreased frit content. Composition MC has approximately 10% tin oxide added to composition MB.

These electrode materials were applied to the ceramic discs to form capacitors. The properties of the capacitors were studied as a function of the electrode material, the ceramic material and the reduction conditions. The electrode materials were screened on, baked at 140-150°C for 15 minutes and fired at 927°C for 30 minutes in a lab tunnel kiln, using a preheat zone at 740°C. In general, composition CB material turns very light in color after firing, in air, indicating reoxidation taking place more rapidly than in the case of commercial grade materials.

Measurements

Resistivities were measured with a 4 - point probe. Because of different shrinkage rates the diameter and thickness of each of the materials used was different after rawfiring and was corrected to evaluate resistivity. The corrected resistivities of the materials are shown. The variation of resistivity with reduction temperature and with the different materials used is also shown.

REOXIDATION STUDIES

It was of interest to study the degree of reduction and the rate of reoxidation of the high purity barium titanate compared with the commercially pure material. For this purpose a number of specimens of both materials were reduced under identical conditions and were reoxidized at different temperatures. Cross sections were made of the specimens by mounting in epoxy and using ultrasonic abrasion. On looking at the specimens under a microscope and using polarized light it was possible to detect the extent of reoxidation and to observe that the high purity material had reoxidized more quickly than the commercially pure material. Reoxidation appears to occur more slowly than reduction. This was

especially true for the commercially pure ceramic material.

It is desirable that the material should not reoxidize too quickly as it may thus be unsuitable for capacitor manufacture. As the high purity material reoxidizes more quickly than the commercially pure material it requires a different firing cycle. The conditions for reoxidation of the ceramic and maturing of the electrode material do not necessarily coincide.

Silver paints normally contain Bi_2O_3 and other constituents such as lead borosilicate etc. These materials readily reduce in a reducing atmosphere and leave discontinuities in the electrodes. Electrode firing at lower temperatures on the other hand gives higher capacitance but poor leakage so that it may be preferable to fire in air diluted with nitrogen.

Nonuniformity of Capacitor Surfaces

The oxidation studies showed on the other hand that there is faster oxidation round the edges of discs and thus porosity is likely to be present which is not observable using ink tests. A small fraction of the commercially pure discs showed porosity around the edges. These specimens were removed from tests.

Similarly the state of reduction will vary gradually from insufficient reduction at P the center to excessive reduction at Q the periphery as shown in fig. 3(B), so that the leakage current will be as in fig. 3(A).

The resistivity and capacity relationship is shown in fig. 3(C) for different states of reduction. Under a given set of reduction conditions, different degrees of reduction corresponded with different degrees of porosity of the individual discs. The cited curves represent the state of reduction of a capacitor which is porous at the edges and becomes less porous as we proceed towards the center. The points P,Q, of figs. 3(A), 3(B), and 3(C) correspond so that the lowest leakage will be at Q and hence the overall breakdown voltage will correspond with the breakdown voltage at Q and will be low.
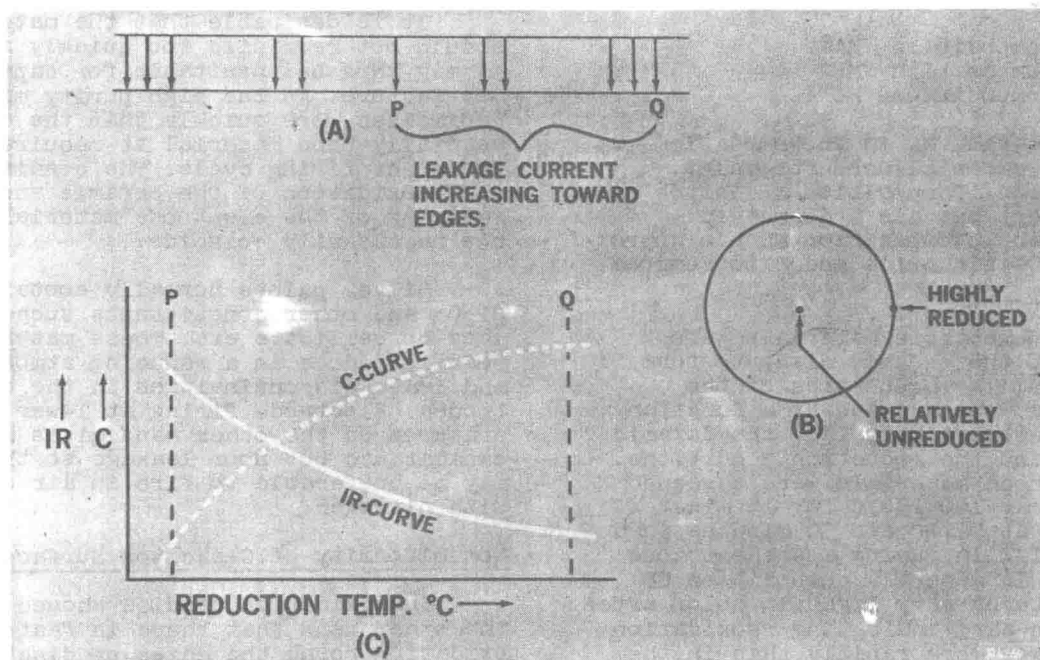
Fig. 3 Variation of leakage with distance from the center of a capacitor disc. (A) Cross-section of a Capacitor, (B) Top View, (C) Leakage curve.

Results

The density, dielectric constant and the dissipation factor are shown as a function of rawfiring temperature in Fig. 4 for material CA. Further information on the properties of this material is given in the literature[1]. The effect of reduction temperature on resistivity of the reduced $BaTiO_3$ is shown in Fig. 5. The high purity material is observed to have a higher resistivity than the commercially pure material. Figs. 6-11 show capacitance and dissipation factor as a function of reduction temperature for $BaTiO_3$ reduced in H_2. Figs. 12-13 show the same information for reduction in forming gas ($10\%H_2$, $90\%N_2$), for electrode material MC. It may be observed from figs. 9-16 that the electrode materials MA, MB, MC affect the high purity material lot 2 in the same way that they affect the commercial purity material. The insulation resistance of the capacitors made from high purity material was higher than that obtained using the commercial purity material. The effect of temperature on the resistance of the reduced material was in agreement with that reported by Saburi[2]. On reoxidation an oxide layer is visible at the center of discs in a plane parallel to the disc faces. Thus reduction is nonuniform.

Discussion

It has been observed during oxidation studies that specimens oxidize more readily round the edges than towards the center of ceramic discs. Specimens have also been observed to reduce more effectively towards the edges of ceramic discs. Density variations in the fabricated ceramic discs indicate that the periphery is more susceptible to oxidation and to reduction resulting in a nonuniform structure for the capacitor device. This condition probably contributes to warpage on firing. Nonuniform oxidation characteristics have been observed even though there is negligible observed porosity around the edges of the disc. Reduction conditions particularly atmosphere produced strains in the materials. These were generally more pronounced in pure H_2. The resistivity measurements support this idea as lower resistivity resulted from reducing in H_2. High purity materials appear to favor oxidation instead of reduction which is the opposite of experience in commercial grade materials.

No attempt had been made to optimize the firing cycle used for reduction or the firing cycle used for electrode fire-on as far as high purity $BaTiO_3$ was con-

cerned. The optimum firing cycle for the high purity material will undoubtedly be different to the optimum cycle for commercial grade materials. The results show that grain size is a very important factor in determining capacitor parameters. The importance of grain size has been known to previous workers and diverse methods of controlling grain size have been used. Hyatt and Laird[3] suggested sintering of prereacted high purity $BaTiO_3$ to produce improved dielectric properties. Harkulich et al[4] and Kiss et al[5] used additions of Ta_2O_5 as a grain growth inhibitor to produce the desired density and grain size. Egerton and Koonce[6] observed that dielectric constants were highly influenced by grain size. Eubank et al[7] reported a two to threefold increase in dielectric constant for higher purity material but do not appear to have made a detailed study of the effect of grain size. On the otherhand they found that the change of capacity with temperature was larger for the purer titanates than for the commercial grade material. Buessem et al[8] suggest that small grain size $BaTiO_3$ is subjected to higher stresses than larger grain size $BaTiO_3$ on cooling through the Curie temperature and that it is this stress which in effect produces the higher dielectric permittivity of small grain size materials. In the present work it was found that high purity materials were sensitive to impurities absorbed during processing. This is in agreement with the observations of Eubank et al[7] that Al and Si are absorbed by high purity titanates during milling with aluminum silicate. Nelson and Cook[9] studied the effect of wet milling in detail and found that the amount of contamination introduced depends on the milling conditions used and is directly responsible for the deleterious effect on properties. Milling time should be as short as is consistent with proper mixing.

Conclusions

The feasibility of making high purity barium titanate capacitors has been demonstrated for the case of the polycrystalline $BaTiO_3$ materials evaluated. Control of process conditions is, however, more critical than when commercial purity material is used. In particular, the microstructure appears to have a controlling effect on the resultant dielectric properties. Of equal importance is the control of the amount of impurities absorbed into the system during processing. The microstructure can be optimized by control of the heating cycles and pressing conditions. Although these tight processing conditions do not provide undue difficulties on a laboratory scale they may cause difficulties in the case of a production run. In such cases a grain growth inhibitor would be useful.

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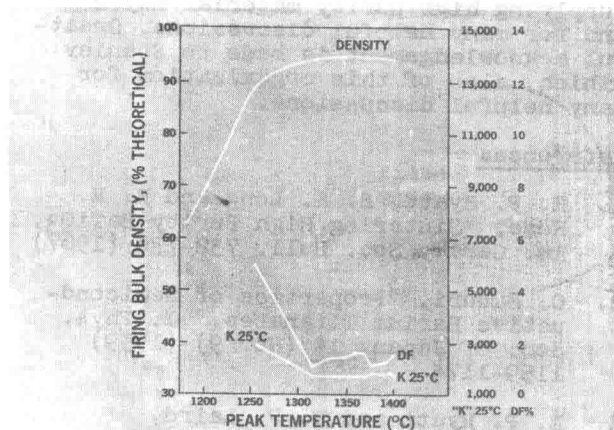
Fig. 4 Physical and Electrical Properties of Material CA as a function of firing temperature.
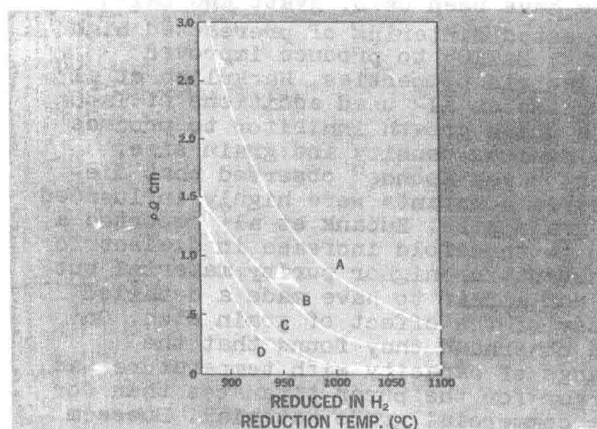

Fig. 5 Resistivity as a function of reduction temperature.
A-Material CB lot 2,
B-Material CA lot 2,
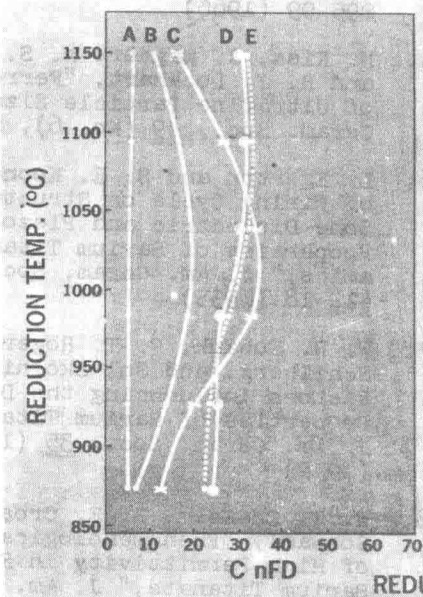C-Material CC,
D-Material CD

Fig. 6 Reduction Temperature vs. Capacity for Electrode Material MA. A-Materials CA, CB lot 1, B-Material CB lot 2, C-Material CA lot 2, D-Material CD, E-Material CC.
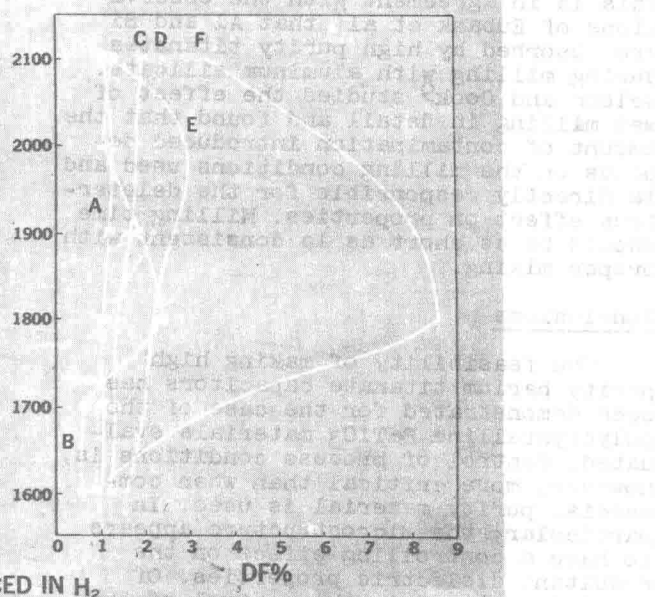

Fig. 7 Reduction Temperature vs. Dissipation Factor for Electrode Material MA. A-Material CA lot 1, B-Material CB lot 1, C-Material CC, D-Material CD, E-Material CA lot 2, F-Material CB lot 2.
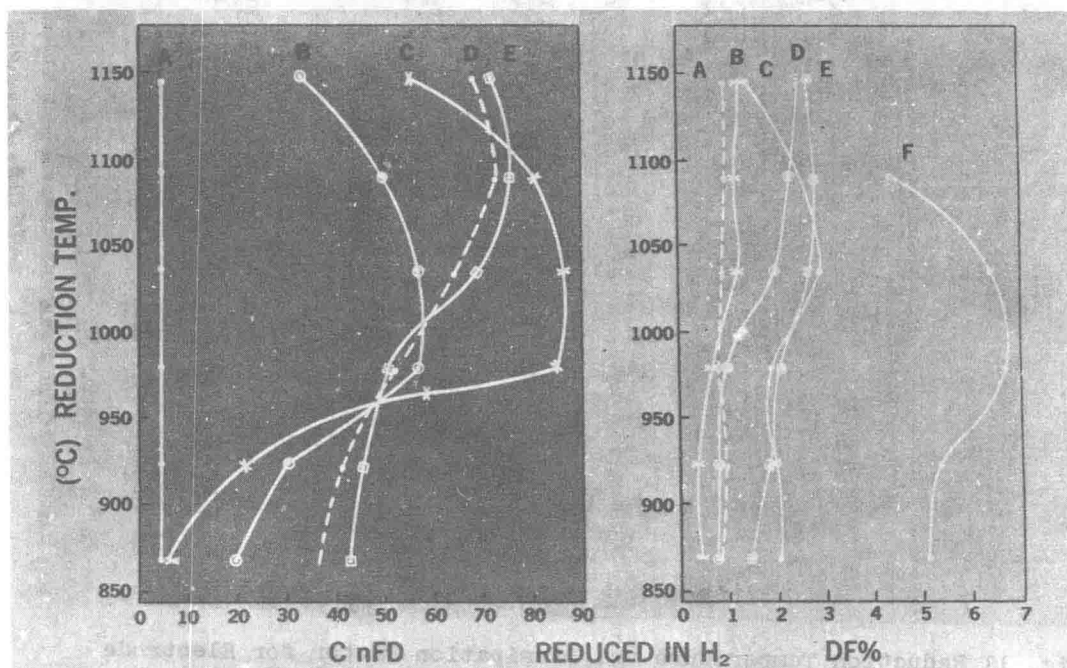
Fig. 8 Reduction Temperature vs. Capacity for Electrode Material MB. A-Materials CA, CB lot 1, B-Material CA lot 2, C-Material CB lot 2, D-Material CC, E-Material CD.

Fig. 9 Reduction Temperature vs. Dissipation Factor for Electrode Material MB, A-Material CA lot 1, B-Material CB lot 1, C-Material CA lot 2, D-Material CD, E-Material CC, F-Material CB lot 2.
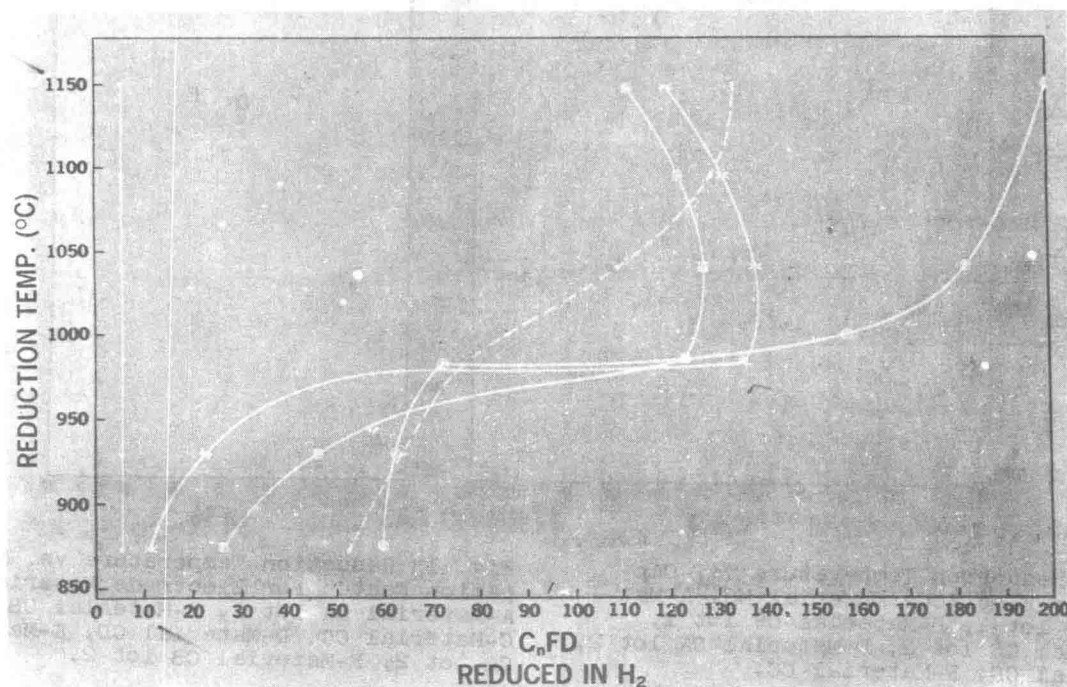
Fig. 10 Reduction Temperature vs. Capacity for Electrode Material MC. A-Materials CA, CB lot 1, B-Material CA lot 2, C-Material CB lot 2, D-Material CC, E-Material CD.

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