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USASRDL Technical Report 2196

PROPERTIES OF HOT-PRESSED BARIUM TITANATE

by

Arthur Brown

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U.S. ARMY SIGNAL RESEARCH AND DEVELOPMENT LABORATORY

FORT MONMOUTH, N. J.

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FIGURES

PROPERTIES OF HOT-PRESSED BARIUM TITANATE

INTRODUCTION

The objective of the program described was to develop a technique for producing a dense, hot-pressed barium titanate sample having an average grain size of less than one and to compare its electrical properties with those of conventionally-fired barium titana

Barium titanate had been hot-pressed by others using graphite dies. Hot-pressing in results in reduced barium titanate ceramic which, upon subsequent oxidation, was subje grain growth. Hot-pressing of cadmium niobate in ceramic dies had previously been den at USASRDL by DeBretteville, et al,[1] and barium titanate had been hot-pressed and son properties reported by Tennery.[2]

Further development of the hot-pressing technique has enabled the authors to produc nonreduced samples of extremely fine grain structure whose electrical properties are of

METHOD

The hot-pressing apparatus consists of an induction furnace used in conjunction wit and die assembly. An over-all view of the assembled apparatus is shown in Figure 1.

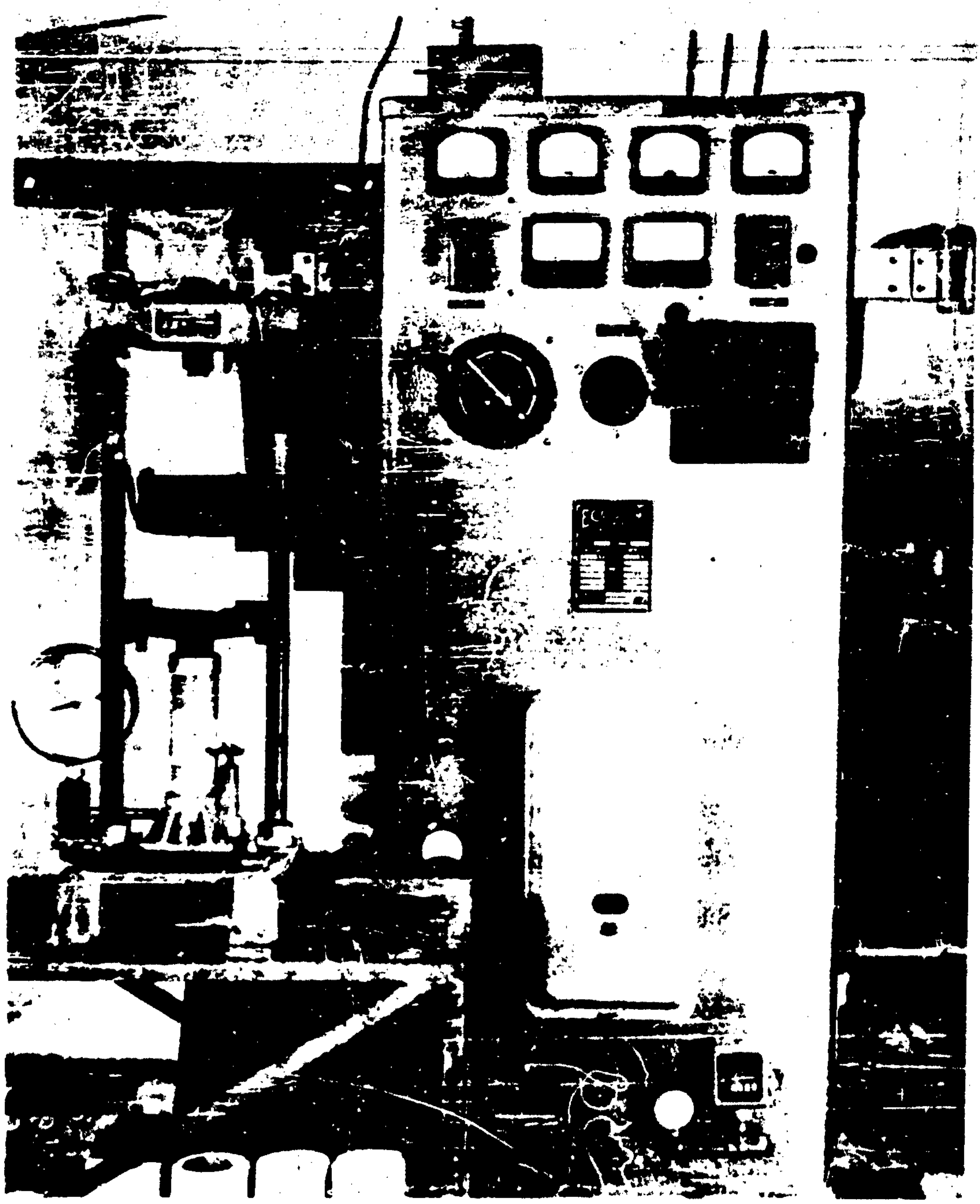
The induction power supply is a 20-kw, 10-kc motor generator, which allows rapid he with good control. The furnace, which was assembled on the platen of the press, was a insulating fire brick cut to fit inside the induction coil and around the die assembly. A tional, manually-operated hydraulic laboratory press was used. The furnace and die ass are shown in Figure 2

The ceramic dies which have proven most effective for our work with barium titanate 100%, stabilized zirconia made slightly porous to improve thermal shock resistance. Ot materials such as alumina and alumina porcelains can also be used with some degree of A stainless steel bushing was shrunk onto the ceramic sleeve to serve as the susceptor add mechanical support.

The method used to prevent adherence of the material being pressed to the ceramic c embed the sample in a relatively coarse zirconia powder (TAM No. 45006). This method sticking to the die and allowed the sample to be ejected easily while hot. The amount c that diffused into the sample during firing has not been determined, but the layer of zirc that adhered to the surface of the sample was easily removed by grinding.

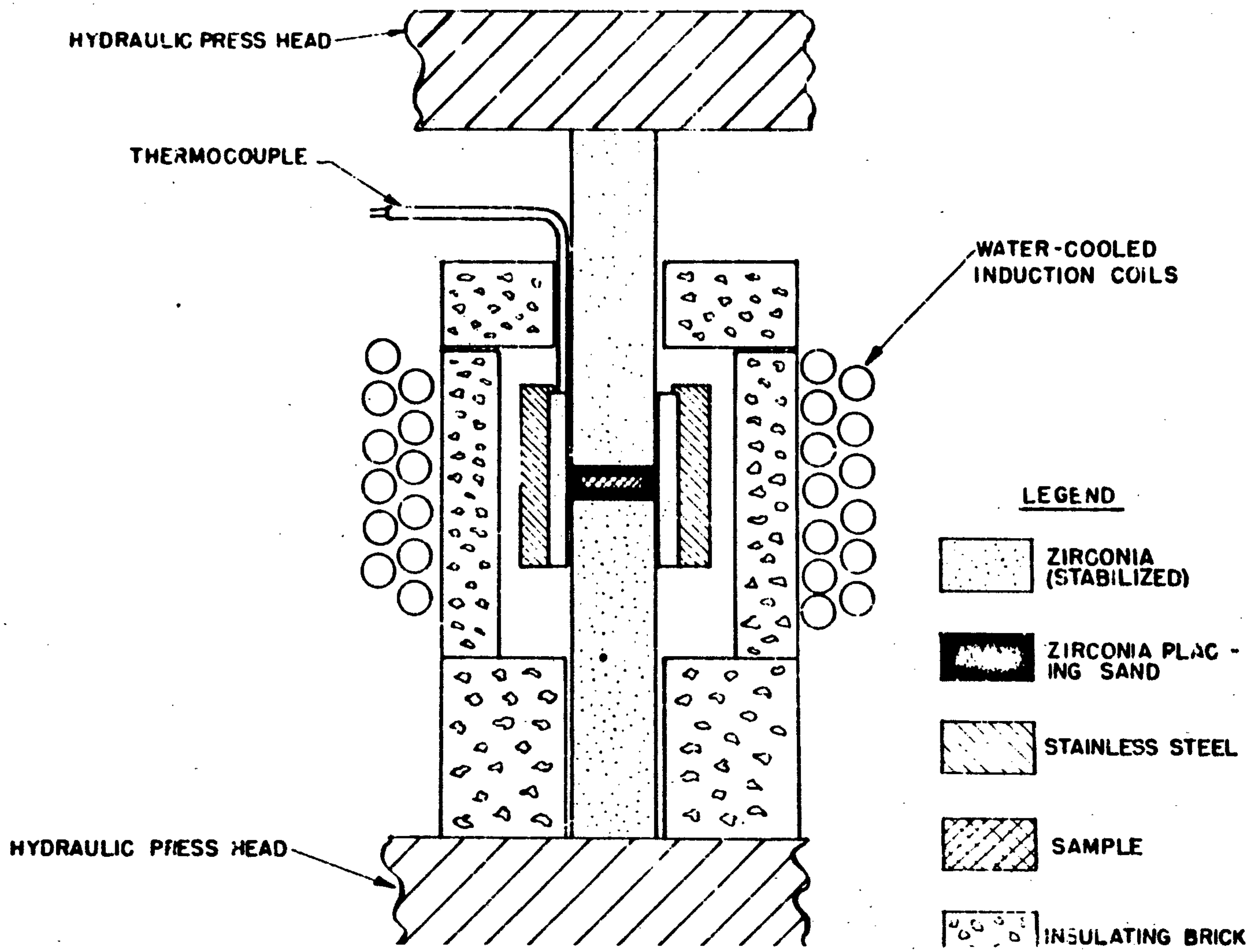
PROCEDURE

A sample disc of barium titanate 1/8 inch smaller in diameter than the zirconia die v preformed at 10,000 psi with no binder. This preformed disc was loaded into the hot-pre in such a manner as to be completely encapsulated in zirconia placing sand. The loade was aligned in the induction coil, and a pressure of 5000 psi was applied and maintaine out the heating cycle. The rate of heating was controlled in such a manner that a tempe 2000° F was reached in ten minutes. The sample was held at this temperature and press twenty minutes and then quickly ejected from the die and buried in vermiculite to cool. cooling, the sample was removed from its zirconia casing, ground to the desired shape, polished.



M-58-315

FIG I HOT-PRESSING APPARATUS


HYDRAULIC PRESS HEAD
THERMOCOUPLE
WATER-COOLED INDUCTION COILS
HYDRAULIC PRESS HEAD
LEGEND
ZIRCONIA (STABILIZED)
ZIRCONIA PLAC - ING SAND
STAINLESS STEEL
SAMPLE
INSULATING BRICK

Other combinations of pressure, time, and temperature of firing were investigated; however, [illegible] above 5000 psi lead to rapid deterioration of the dies, and a significantly lower temperature or shorter time does not yield a fully vitrified body.

CHARACTERISTICS OF HOT-PRESSED $BaTiO_3$

Density and Microstructure

The polished samples had a yellowish color that is characteristic of nonreduced barium titanate. Fractured surfaces were glassy, an indication of the high density and fine grain size. Density measurements, made by displacement, averaged 5.9 gm/cc, some samples measuring as high as 6.0 gm/cc. When examined under 500 X magnification, polished samples exhibited no apparent grain structure before or after etching.

After careful polishing, samples were etched in a solution of 0.5% HF and 1.0% HNO_3, and platinum shadowed carbon backed replicas were prepared and examined with the electron microscope at magnifications up to 20,000 X. It was found that due to the small grain size a satisfactory polishing and etching technique could not be developed.

Fractured surfaces were replicated [illegible] all electron micrographs are of unetched fractured surfaces. The grain size in the hot-pressed barium titanate was found to be less than 1 micron (Figure 3). Figure 4 illustrates the large grain size observed in a fractogram of kiln-fired barium titanate.

The fine microstructure observed in the hot-pressed samples is attributed to the fine particle size of the starting material, and to the predominance of plastic flow as the mechanism of sintering under these conditions. The average particle size of the barium titanate used (TAM FT grade) was 0.5 micron. These particles were found to be agglomerated in such a manner that they indicated a particle size distribution of 1 to 3 microns by sedimentation methods. Electron micrographs showed the actual particles to be 1 micron and less (see Figure 5), essentially the same size as those appearing in the hot-pressed samples.[3] This indicates that there was no significant grain growth during densification and that hot-pressing offers a method to be used to control grain size.

Electrical Characteristics

The electrical properties of hot-pressed barium titanate samples prepared as above were quite striking when compared to those of conventionally prepared samples. The dielectric strength has been found to be [illegible] volts per mil as compared with values of 100 to 200 volts per mil, usually observed in conventionally processed barium titanate samples 1/10 inch thick.

Figure 6 illustrates the differences observed in measurements of the dielectric constant and dissipation factor with temperature. The reduction in the peak of the dielectric constant in the vicinity of the Curie temperature is attributed to the fine grain size. At room temperature the dielectric constant is above [illegible] and is independent of the orientation of the sample with respect to the direction of the forming pressure. No dependence of K on frequency was found from [illegible] cps to [illegible]. Figure 7 depicts the variation of dielectric constant with time under static room temperature conditions for conventional and hot-pressed $BaTiO_3$. The samples were de-aged by heating to [illegible] °C for [illegible] minutes; aging time was measured from the moment of removal from the oven. Since the aging of the dielectric constant has been reported to be due to a gradual reorientation of the ferroelectric domains, the results of this measurement [illegible] imply that the domains in the hot-pressed material were relatively stable.[4,5] This degree of stability has not been achieved in conventional K [illegible] bodies.

FIG 3 FRACTURED SURFACE OF HOT-PRESSED $BaTiO_3$

FIG 4 FRACTURD SURFACE OF KILN-
FIRED $BaTiO_3$

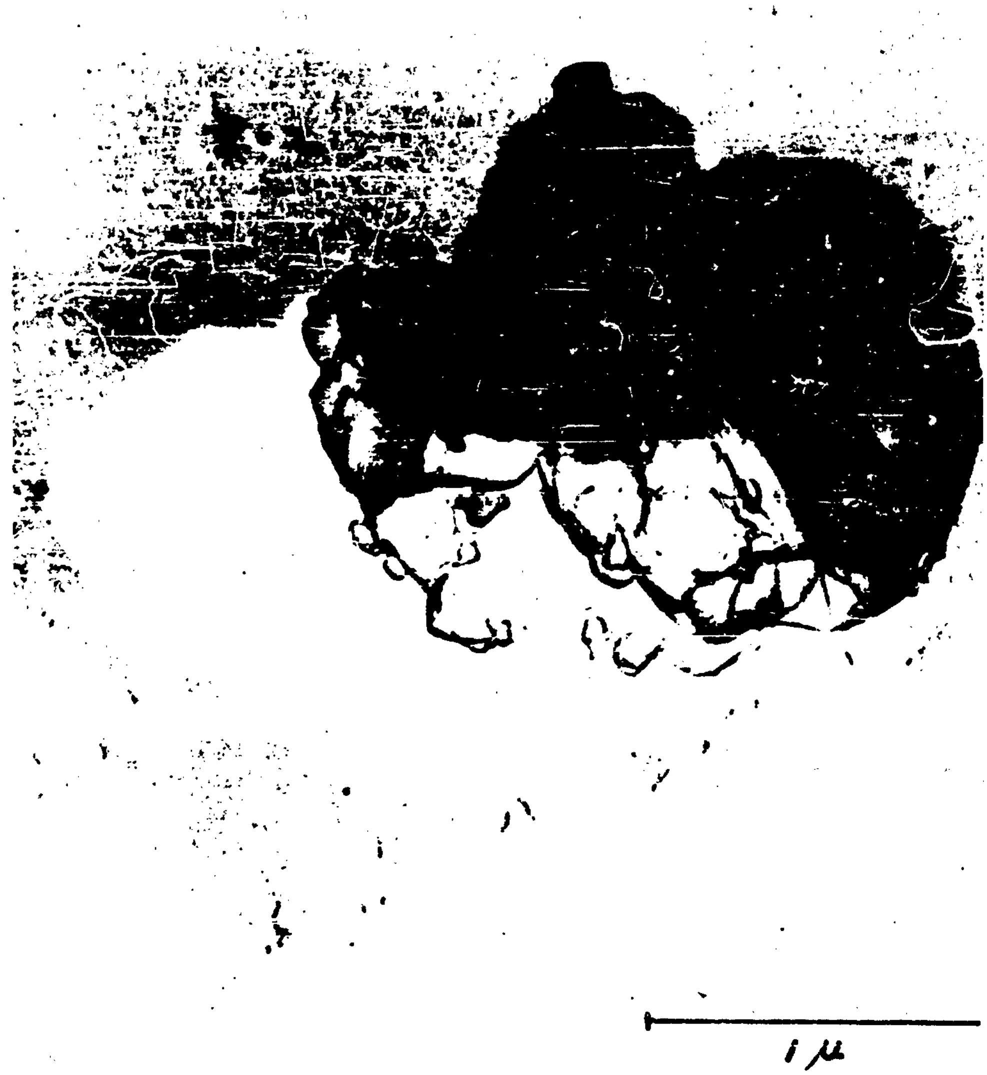


FIG 5 PARTICLE REPLICA OF $BaTiO_3$ POWDER

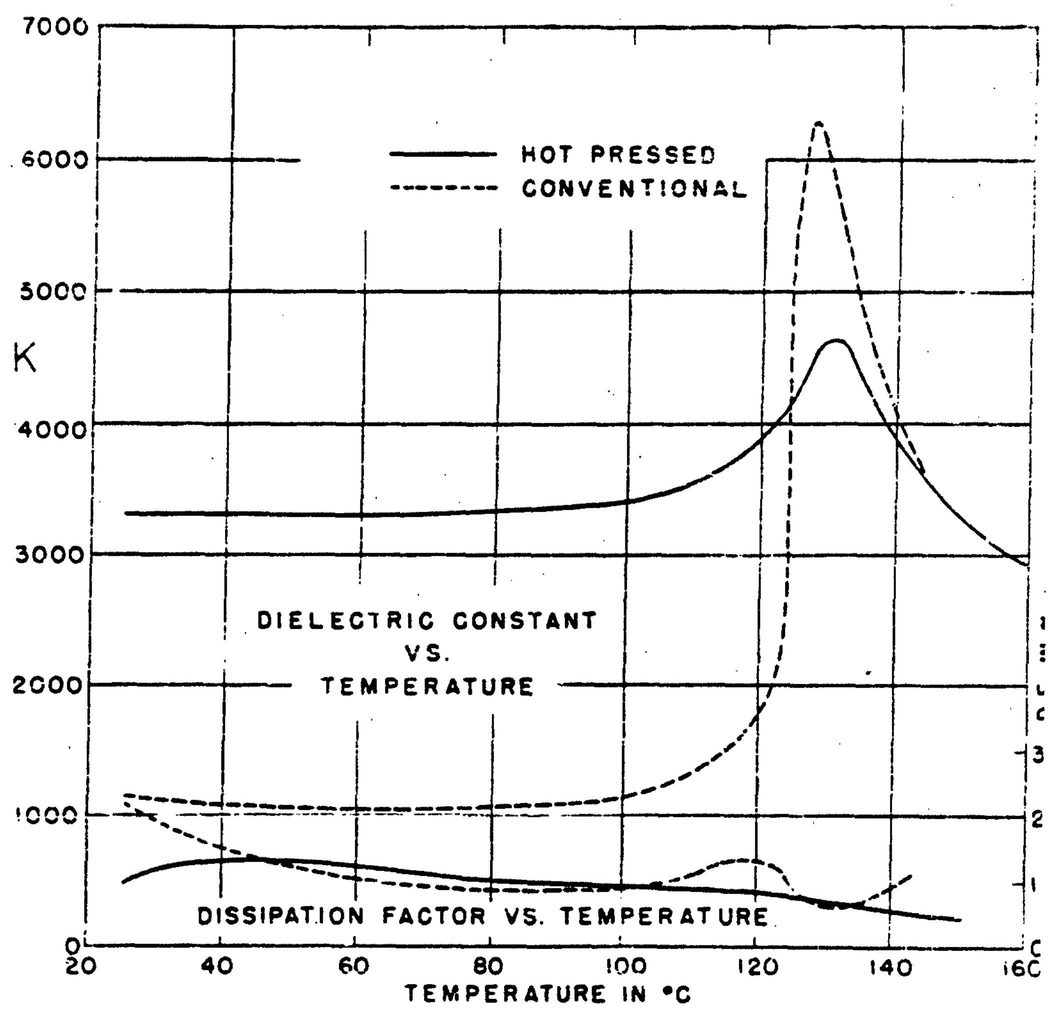
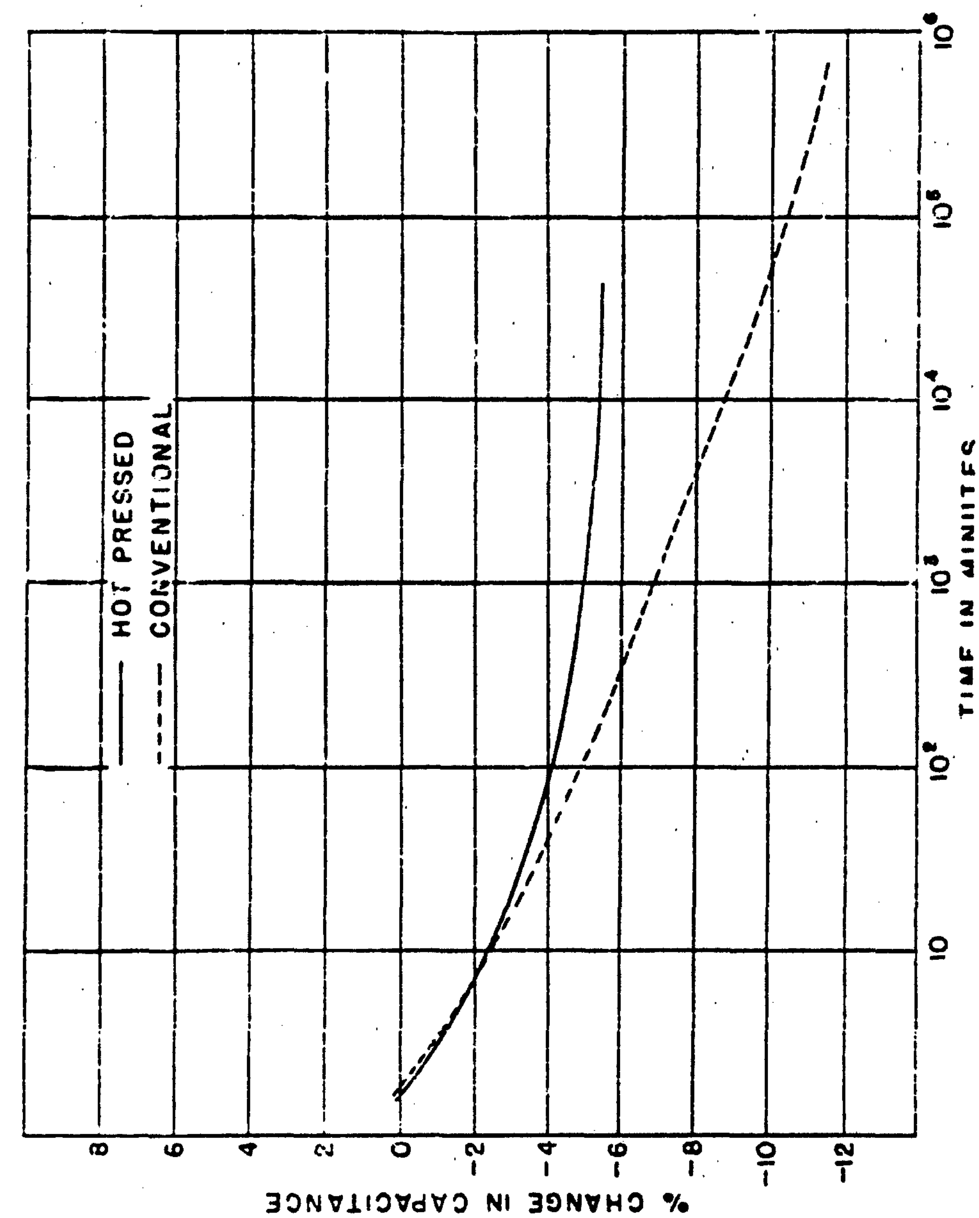


FIG 6

DIELECTRIC PROPERTIES OF TWO TYPES OF BARIUM TITANATE



HOT PRESSED
CONVENTIONAL
% CHANGE IN CAPACITANCE
8
6
4
2
0
-2
-4
-6
-8
-10
-12
TIME IN MINUTES
10
10^2
10^3
10^4
10^5
10^6

An attempt was made to pole hot-pressed samples of $BaTiO_3$ by applying a high DC field at room temperature or while cooling from 120°C, but little or no piezoelectric response was observed.

CONCLUSIONS

The hot-pressing technique described in this report produced a dense, nonreduced barium titanate sample with no apparent grain growth. The limiting factor in producing a fine-grained $BaTiO_3$ body was in the particle size of the raw materials. A project has been initiated to produ a $BaTiO_3$ powder with an average particle size of less than 0.1 micron.

The dielectric properties of these materials were greatly enhanced by small crystallite size, but the piezoelectric response was almost completely eliminated. These results show the significance of the effect of density and grain size on the ferroelectric properties of barium titanate and indicate that an extension of this study over a wider range of particle sizes, particularly below 0.1 micron, might be expected to produce new or improved electrical properties in ferroelectric materials.

ACKNOWLEDGMENTS

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3. Fine Grain Structure

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