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HIGH DIELECTRIC CONSTANT MATERIAL

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The present invention relates to new and improved dielectric compositions, and in particular, to dielectric compositions which are useful for piezoelectric purposes.

For the last ten years or so, various titanate compositions have been used as the ceramic dielectric in so-called printed circuit type capacitors and integrated circuit components. Some time ago, it was discovered that dielectrics falling within this category, especially barium titanate, could be made to possess piezoelectric properties by subjecting them to a D.C. field over a long period of time. Numerous modifications of this basic procedure for polarizing titanates have been developed. Most frequently, the actual polarization is accomplished while subjecting the body to a temperature above 20° C., yet below the Curie point of the ferroelectric. Alternatively, barium titanate and other related ferroelectrics may be polarized by subjecting them to a D.C. field while cooling the same from above the Curie point.

All of these polarization attempts have been more or less satisfactory, but by none of these procedures has it been possible to obtain as complete and as satisfactory a set of dielectric and piezoelectric properties as is usually desired. In an attempt to produce compositions having highly advantageous dielectric properties, it has been proposed to utilize single crystals of materials, such as barium titanates, for use as dielectrics or as piezoelectric elements. Single crystals of these materials are rather difficult to grow and, in addition, they have the defect that they contain a multitude of crystalline domains prior to the polarization and/or orientation. The presence of a multitude of domains within such unitary bodies makes the polarization of the final material somewhat more difficult than is desired, and also, prevents the obtaining of a final ferroelectric body which is completely free from strain and which possess the maximum in piezoelectric properties.

It is an object of the present invention to improve upon the aforegoing and related prior art products and processes. A further object of the invention is to produce new and improved dielectric and piezoelectric compositions having very advantageous properties. Further objects of the invention, as well as the advantages of it will be apparent from the following specification, as well as the appended claims.

Briefly, the new compositions in the present invention are obtained by following four principal separate steps, two of which may be combined if desired. These are:

(1) Grinding powder of a ferroelectric until it is approximately the size of single domain crystals as opposed to single crystals.
(2) Forming these powders into a unitary body while subjecting them to the influence of an electrical field.
(3) Firing the so-formed bodies at an elevated temperature so as to produce a fused mass.
(4) Orienting the so-fused mass with the aid of an electrical field so as to produce piezoelectric characteristics.

If desired, the firing and orienting steps can be combined into a single procedure in accordance with one of the preferred embodiments of the invention.

A distinguishing feature of this invention, as will be seen from the above summary, as well as the rest of this application, is the fact that the new compositions produced are composed of completely homogeneous single domain crystals. Such crystals differ decidedly from the common single crystals of such materials as barium titanate, inasmuch as single crystals or barium titanate contain a multitude of crystalline domains. Obviously, the new compositions are far removed from the prior polycrystalline bodies, such as are commonly used commercially at the present time. These new compositions are quite advantageous because of their improved piezoelectric characteristics, and high dielectric constants, and because they possess a virtually square hysteresis loop. The new materials herein described have a greater output than the presently known related materials, and further possess a much faster frequency response than these materials. They are comparatively inexpensive and readily produced.

STARTING MATERIALS

Barium, strontium, lead, and other related titanates derived from virtually any source may be used with the present invention. Because of its cheapness, availability, etc., it is preferred to use the finely ground barium titanate powders marketed by a number of firms, such as Titanium Alloys Manufacturing Company or E. I. du Pont de Nemours & Co., Inc. Similar satisfactory materials can be produced by fusing barium chloride and titanium dioxide together or by other means known to the art. Even single crystals having a multitude of crystalline domains can be used as a starting material with the present inventive concept. All of the materials used preferably have a high degree of purity and contain less than 1% of undesired ingredients. In order that there will be substantially no stresses set up, this applied even to impurities of related elements entering into isomorphous ferroelectric crystalline structures.

One novel method of preparing starting materials for the present invention consists of reacting a soluble inorganic compound with a titanate ester. As an example of this, a concentrated solution of brium chloride or other similar soluble salts may be intermixed with a titanate ester, such as butyl titanate so as to form a fine precipitate of barium titanate, and/or so as to form a suspension of colloidal or macro colloidal characteristics depending upon the reaction conditions. Colloids obtained in this way can be broken by established known techniques, and the resulting solids, whether obtained by bleaking a colloid or precipitation, can be separated and purified in accordance with known procedures, such as filtration. The solids produced as discussed in this paragraph are normally substantially all simple domain crystals which require little, if any, subsequent grinding to be used with the invention.

GRINDING

The starting materials herein indicated can be ground to substantially single domain crystals by any of a variety of procedures, most of which are established in diverse arts. One very common procedure involves the use of grinding apparatus, such as, for example, ball or rod mills for a period of from one day to about three weeks. Another procedure which can be adapted to the present invention involves the shooting of previously finely ground particles against a hard surface in an air stream,

This procedure is roughly analogous to the use of various sand blasting apparatuses to grind rather fine powers into single domain crystals.

A still further procedure which produces exceedingly desirable results involves the rapid quenching of heated particles of barium titanate, and the subsequent grinding of the so-quenched material. The more drastic the quenching, the more finely divided the final product obtained, and hence, the higher the single domain crystalline content of this product. As an example of this type of procedure, barium titanate may be quenched from a temperature of 2200° C. by immersion into a vat of water slightly above the freezing point. Alternatively, the quenching media can even be such a low temperatured media as an acetone and Dry Ice mixture.

A further procedure which can be used in grinding consists of producing very compact pellets of barium titanate containing a small proportion of a volatile ingredient, such as water, heating these pellets while subjecting them to considerable pressure, and then subsequently releasing this pressure so as to enable the volatile ingredient to undergo a terrific sudden expansion in size. This type of a procedure is roughly analogous to the puffing of a wheat kernel in the manufacture of puffed wheat, and suitable apparatus may be found in any of the earlier Anderson patents for puffing starches.

Frequently, most advantageous results are obtained by combining one or more of the above grinding procedures. Those skilled in the art are readily able to work out the most desirable method for grinding a ferroelectric powder from any given source with a minimum of experimentation.

FORMING

After the barium titanate has been ground into substantially single domain crystals, it is formed into a self-supporting mass while being subjected to a D.C. field of from 5 to 100 volts per unit of a formed pellet thickness. This formation can take place with air as the suspending media for the individual crystals, and with the use of pressures of from about 500 to 15,000 p.s.i. With such procedures, it is best to use a small proportion of an organic volatilizable binding composition, such as, for example, polyvinyl alcohol gum tragacanth, gum arabic, potato starch, or the like to aid in holding the individual particles in a unitary relationship. These binding materials may be admixed with the single domain crystals in any of a number of known procedures, such as, for example, by the use of a tumbling drum. Alternatively, they can be admixed with the individual particles during the grinding procedure.

For many purposes it is preferred to use a liquid suspending vehicle during the formation. When this is done, apparently a substantially higher proportion of oriented single domain crystals are found in the formed body than are found when the procedure of the preceding paragraph is used. Water is a quite satisfactory suspending media. However, other materials, such as, for example, monomeric styrene, solutions of polyethylene in organic solvents, such as, acetone; silicon oils, or the like can all be used with advantageous results. When the suspending composition is capable of forming a polymer as by heat polymerization or by volatilization of a solvent, such a polymer can be produced so as to serve in substantially the same regard as the various binding materials previously indicated. With such materials as styrene, a small amount of heat and/or organic peroxide catalyst can be employed to aid in the polymerization.

Slurries of single domain barium titanate crystals as indicated are preferably cast onto a porous mold while being subjected to a D.C. field, and are allowed to dry in this mold while the field is maintained. One very satisfactory mold material is common plaster of Paris. With it, approximately the same slurry concentrations are (of from 5 to 15%) normally employed. If desired, volatile

dispersing agents, such as carboxy methyl cellulose can be incorporated within such slurries. If desired, heat up to about 300° C. and/or pressures up to about 15,000 p.s.i. can be used in conjunction with a slip as indicated. In the production of very thin films, an impervious matrix is preferably employed instead of a porous body as discussed above. Gravity settling produces highly satisfactory results in the formation of such thin bodies. Also, various thin layers can be placed upon a number of conductive base materials, such as, for example, graphite, by the use of electrophoretic attraction. With such thin bodies, the impervious supports are, in general, burned off of the single domain crystal layer during the subsequent firing operation.

FIRING

The actual firing procedure employed with the present invention is a comparatively uncritical item. In general, temperatures of from about 2000 to about 3000° F. are employed for periods of from about 10 minutes to 6 hours. In a similar manner, the precise atmosphere employed during this step with any of the ferroelectrics falling within the scope of this specification is a relatively uncritical item. For many purposes, it is, however, preferable to control this atmosphere so that it contains a proportion of oxygen which is sufficient to combat any tendency of the dielectric material to give off or absorb oxygen during the actual heating and the following cooling so that a stoichiometric product is obtained. The intermixing gas used with oxygen in any of these cases is preferably of an inert nature and can conveniently be nitrogen. It will be realized by those skilled in the art that even a small deviation from the stoichiometric proportions which could be caused by the use of a relatively strong oxidizing or reducing atmosphere with any of the ceramic ferroelectrics herein disclosed could produce a substantial change in the properties of the final compositions.

Although the cooling rates employed following the firing step indicated are comparatively uncritical, it is best to avoid rapid cooling or quenching so as to avoid the creation of stresses or strains of any type. With barium titanate bodies formed of substantially single domain crystals, this cooling can be as rapid as 10° C. per minute without any material strain being created.

ORIENTATION

If desired, the firing step indicated in the preceding paragraph can be carried out with the individual dielectric layers being subjected to a D.C. field of from about 5 to 100 volts per mil of dielectric thickness. However, this orientation can be accomplished after the firing step in accordance with the procedures known to the art with the same field strengths. One common orientation method is shown in the Gray Patent 2,486,560; another is in the Cherry Patent No. 2,538,554. Frequently, it is desired to conduct the orientation during the initial cooling of the fired bodies down to room temperature, particularly as these bodies pass through the Curie point of the ferroelectric which, as previously indicated, is practically always barium titanate.

One advantage of polarizing this ferroelectric at all times prior to, during, and following the firing operation is that there is little chance of any type of stress or strain beting set up within the final composition due to a transformation of the ferroelectric from a cubic to a tetragonal state. This is a preferred procedure with the invention. As the temperature is lowered past the Curie point, such a change in crystalline structure as normally accompanies the polymerization of a barium titanate composition is disadvantageous because a crystal under these conditions is slightly stressed due to change in dimensions which accompanies this variation in crystal structure.

It will be realized by those skilled in the art that the inventive concept disclosed herewith is capable of wide variation within the scope of this disclosure. All modifi-

cations, alterations, etc. herein discussed or indicated are to be considered as part of this inventive concept insofar as they are defined by the appended claims. As examples of the various procedures coming within the scope of this case, the following specific examples as required by the Patent Rules of Practice are attached hereto. These examples are not to be considered as limiting the inventive concept in any way.

Example 1

Barium titanate powder purchased from Titanium Alloy Division of the National Lead Company, having a mean particle size of 2 microns and arranged in particle diameters in approximately .1 micron to 45 microns, was ground in a common laboratory ball mill until less than 5% of the barium titanate particles were greater than about 1 micron in diameter. This powder was then further milled in the same ball mill with 3% by weight of polyvinyl alcohol for 12 hours so as to coat the individual titanate particles as a further aid to subsequent forming.

The so-called powder was placed in a thin circular mold having a diameter of approximately 1.5 inches in an amount sufficient to form a final pressed pellet approximately 10 mils thick. The mold was provided with electrodes upon the bottom of the cylinder and upon the top plunger. A voltage of approximately 70 volts per mil of thickness was applied across these electrodes for a period of one-half hour. At the end of this time, with the voltage being continued, the particles were formed into a pellet with a pressure of approximately 5,000 p. s. i. which was gradually applied so as to reach the maximum pressure at the end of five minutes. The pellet formed in this operation was then carefully removed so as to avoid any damage by breaking, and was fired at a temperature of about 2350° F. in nitrogen for one-half hour. At this point, it was useable as a highly satisfactory dielectric, but was polarized by being subjected to a D.C. field of 70 volts per mil of thickness for a period of 15 hours at a temperature of 80° C.

Example 2

Particles obtained by fusing stoichiometric proportions of barium chloride and titanium dioxide together with a blowtorch were quenced immediately following their formation by being dropped into a large excess of water at about 35° F. The resulting particles were then taken out of the water and milled in a common laboratory ball mill for a period of approximately 5 days. At the end of this time, these particles were placed in the mold indicated in the preceding example to a loose, uncompacted depth of ¼ inch and polarized at 50 C. for a period of one-half hour. At the end of this time, with the polarization being continued, a pressure of approximately 12,000 p. s. i. was applied gradually over a period of 30 minutes to form a unitary pellet. This pellet was removed from the mold and fired at a temperature of 2,500° F. for a period of one hour while being subjected to an electrical field of approximately 20 volts per mil thickness. The so-fired pellet was then further polarized by being subjected to an electrical field of the same field strength for a period of one hour at a temperature of 60° C.

Example 3

Stoichiometric proportions of barium chloride and butyl titanate were admixed in a container holding 500 millimeters of water. A quasi colloidal suspension was obtained which was immediately filtered through filter paper, washed with distilled water, and removed and mixed with distilled water so as to form a 10% slurry. This slurry was then cast into a quarter inch deep plaster of Paris mold approximately 1 x 2 inches in rectalinear dimension to a dept of approximately 3/16 inch. The bottom of this mold was provided with a porous electrode approximately 1/16 inch below the bottom of the plaster of Paris. A plaster of Paris plunger designed to be used with the apparatus which was provided with a similar electrode about 1/16 inch below its lower surface was inserted into the mold under about 5 p.s.i. pressure after a period of approximately 1 day's settling, and a D.C. field of approximately 50 volts per mil of thickness was maintained across the two electrodes for the next 24 hours. At the end of this time, the entire mold structure was heated in a laboratory oven with the electrical field being maintained at 70° C. for a period of another 24 hours. At the end of this time, the resulting leather-hard barium titanate pellet was removed and fired at 2200° for ½ hour in accordance with established ceramic thicknesses. It was then cooled slowly at a rate of approximately 10° C. per minute per minute until the temperature of about 150° C. was reached. At this point, the so-fired pellet was subjected to a D.C. field of approximately 30 volts per mil of thickness, and further cooled to 40 C. at a rate of 5° C. per minute.

What is claimed is:

1. A process for making a ferroelectric member, said process being characterized by the steps of providing a slip of finely divided ferroelectric ceramic particles having substantially single domain crystal structures, subjecting the slip to a crystal-orienting electric field, drying and firing the oriented material to sinter the particles together and form a coherent body and then electrically polarizing the resulting body.

2. A process for making a ferroelectric member, said process being characterized by the steps of providing barium titanate ceramic of substantially single domain crystal structures of less than one micron in size, then shaping said structures into bodies while under the influence of a D.C. field to align the crystalographic axes of said structures, and then sintering and electrically polarizing said bodies.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,888,737 June 2, 1959

Preston Robinson

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 48, for "brium" read -- barium --; column 4, line 64, for "beting" read -- being --; column 6, line 8, for "dept" read -- depth --; line 23, after "2200°" insert -- F. --; line 25, strike out "per minute", second occurrence; line 29, for "40 C." read -- 40° C. --; same column 6, line 35, for "electric" read -- electrical --.

Signed and sealed this 17th day of November 1959.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

UNITED STATES PATENT OFFICE

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