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[31] **1,614,605**

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[54] **DIELECTRIC CAPACITORS WITH INNER BARRIER LAYERS AND LOW TEMPERATURE DEPENDENCE**

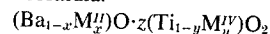
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317/231, 29/571
[51] Int. Cl. **H011 3/06,**
H011 3/22
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237, 230, 231, 233

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ABSTRACT: Dielectric capacitor structures (and method of making the same) comprising a plurality of bound together crystallites having a barium-titanate perovskite lattice structure of the general formula:



which includes at least two different doping substances, one of which predominantly effects N-conductivity in the interior of the crystallites and the other which predominantly effects P-conductivity on the surface of the crystallites. M^{II} is selected from the group consisting of Ca, Sr, Pb, Mg and mixtures thereof; M^{IV} is selected from the group consisting of Zr, Sn and mixtures thereof; x and y are numerals ranging up to one; z is a number ranging from 1.005 to 1.05 the first doping substance is selected from the group consisting of Bi, Ce, La, Nb, Nd, Pr, Sb, Sm and Ta; and the second doping substance is selected from the group consisting of Cu, Fe and Mn.

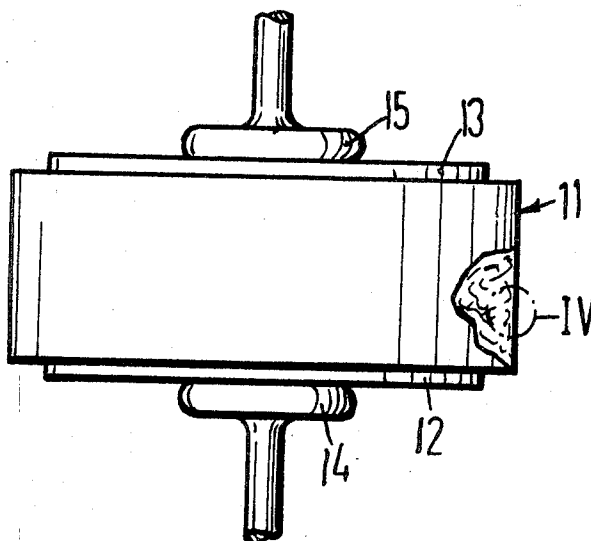


Fig.1

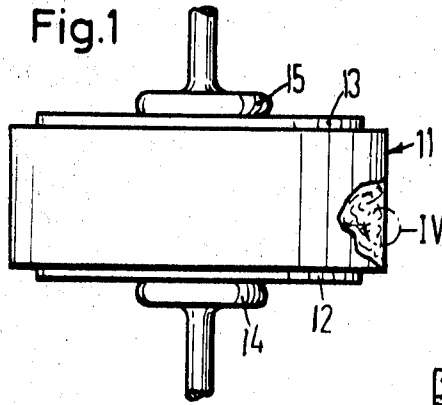


Fig.2

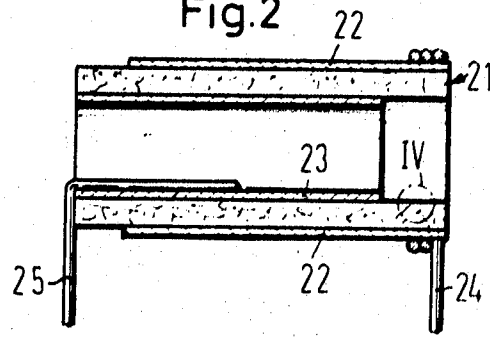


Fig.3

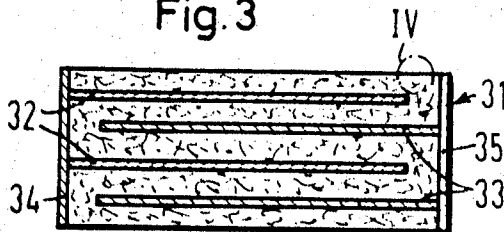
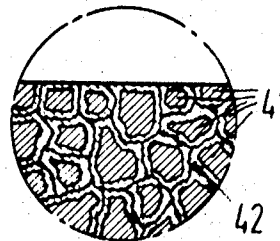


Fig.4



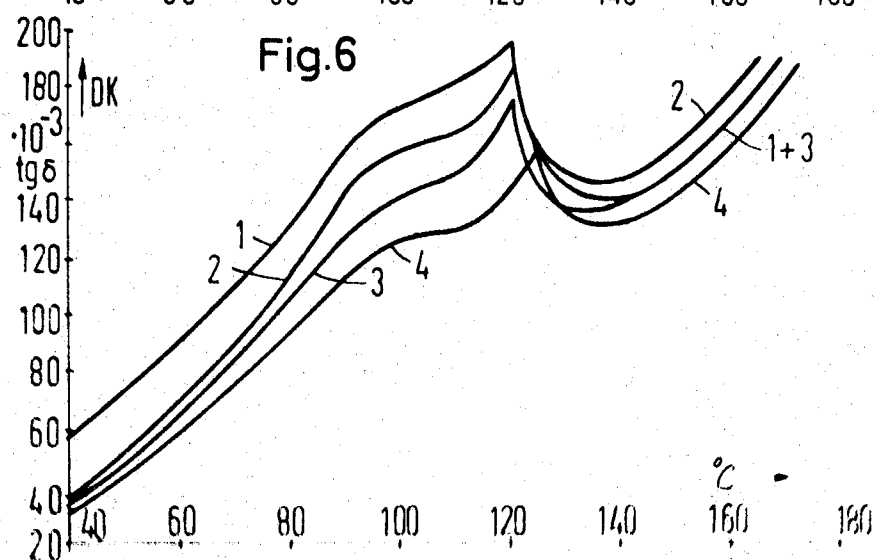
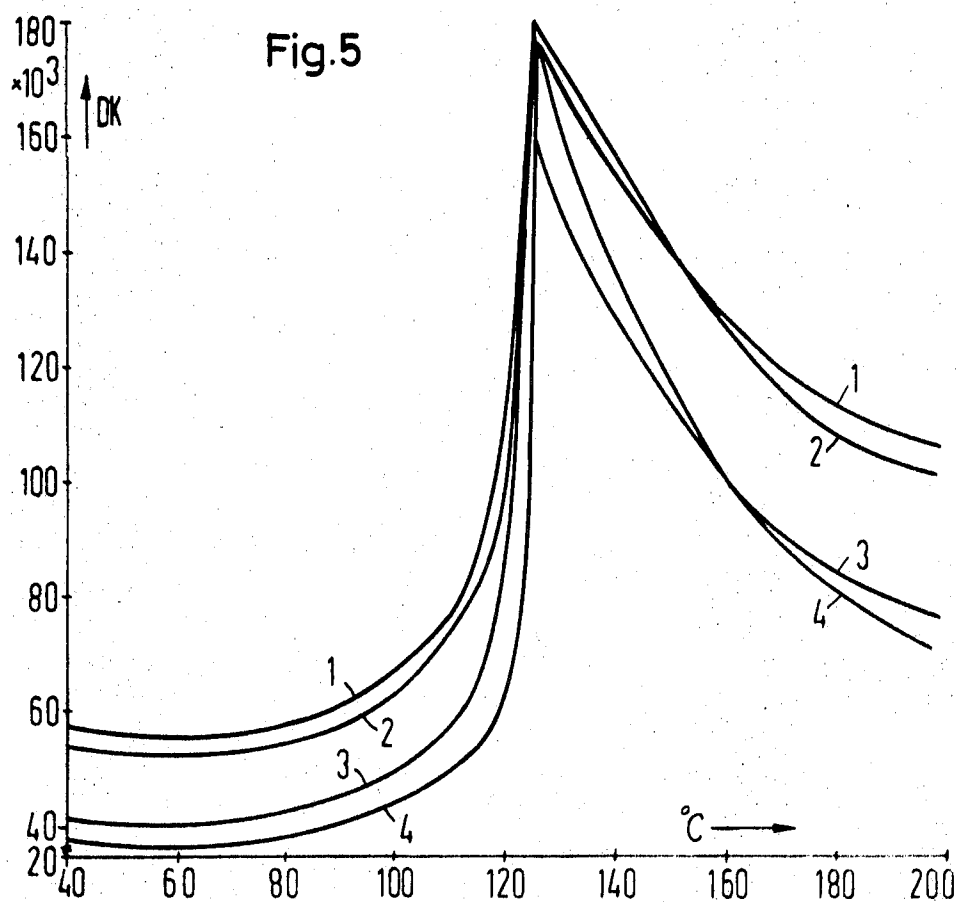
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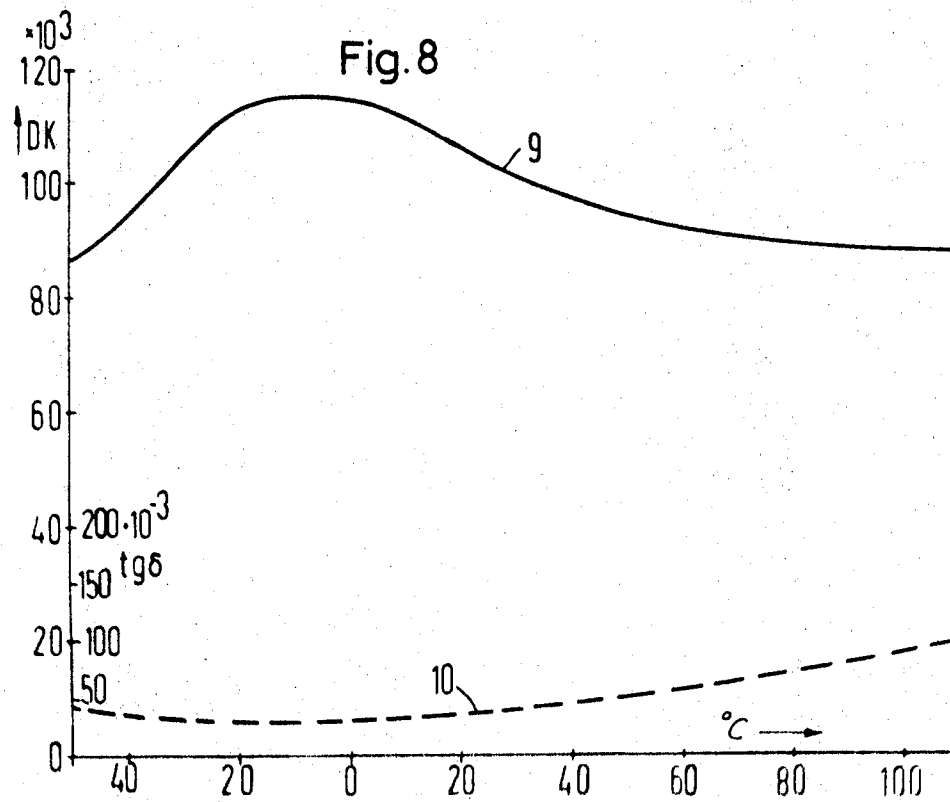
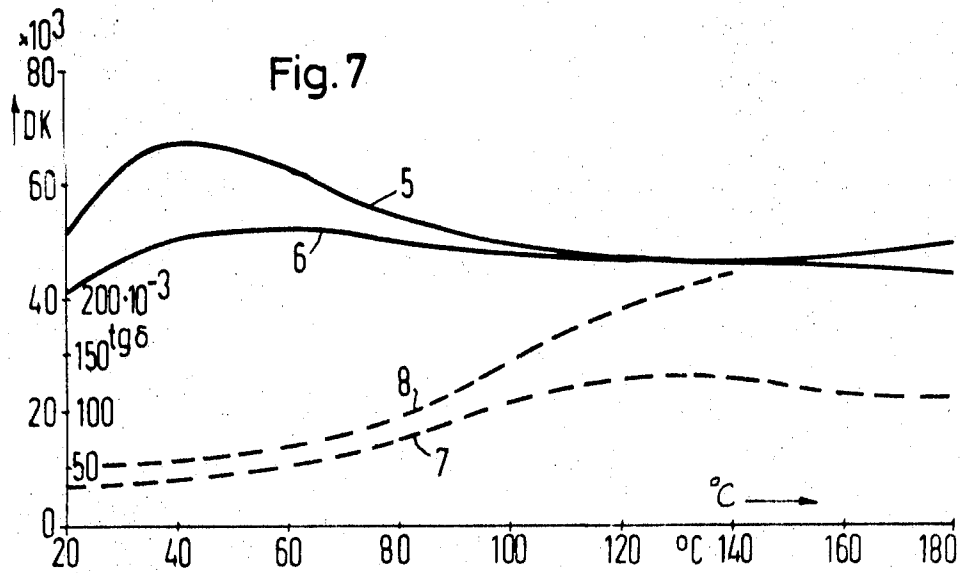


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DIELECTRIC CAPACITORS WITH INNER BARRIER LAYERS AND LOW TEMPERATURE DEPENDENCE

The invention relates to dielectric capacitor bodies having inner barrier layers, more particularly the invention relates to dielectric capacitor materials and bodies composed thereof having inner barrier layers and a low temperature dependence.

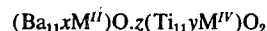
Electric capacitors, which heretofore have been referred to as "barrier-layer capacitors" have a chemically reduced ceramic body generally composed of barium-titanate materials having dielectric layers therein formed through a reoxidation at the capacitor body surface. A disadvantage of these conventional "barrier-layer capacitors" is that one can easily detect the thickness of the dielectrically effective layer at the surface of such bodies. This materially limits the application of such barrier-layer capacitors. Another disadvantage of the heretofore available barrier-layer capacitors (formed through reduction and surface reoxidation of a ceramic body manufactured in a conventional manner), is that they exhibit extremely small dielectric strength. Further, where an operating voltage of more than 10 v. is contemplated, such known barrier-layer capacitors cannot, generally, be utilized.

Attempts have been made to localize the barrier layers formed through reoxidation at the surface of the crystallites. However, even in such so-formed crystallites, an operating voltage of only few volts is possible. Dielectric capacitors of the type described hereinbefore are disclosed, for example, in French Pat. Nos. 1,472,425 and 1,471,752 (owned by the instant assignee) and attention is directed thereto for additional details thereof. Generally, these disclosures suggest that barium-titanate materials are doped with, for example, Sb and combined with certain portions of copper or iron.

Dielectric capacitor structures having inner barrier layers must have the interior of the crystallites as conductive as possible. In instances where known doping materials are utilized, certain maximum quantities, in accordance with recognized teachings in the art, i.e. O Saburi, "Journal of the Physical Soc. of Japan," vol. 14, No. 9, Sept. 1959, pp. 1159-1174, particularly page 1173, and W. Heywang, "Journal of the American Ceramic Soc.," vol. 47, No. 10, Oct. 1964, pp. 484-490 of such doping substances are necessary to achieve a maximum conductivity in barium-titanate materials. From these teachings it becomes apparent that for any of the known doping substances effecting N-conductivity, a particular optimum quantity or amount thereof must be utilized to attain the highest conductivity in barium-titanate crystallites containing the same. This highest conductivity is generally referred to as the maximum doping quantity for that particular substance. For example, for antimony (Sb) this quantity is about 0.1 percent by weight calculated as Sb_2O_3 and for lanthanum (La) the quantity is about 0.3 percent by weight calculated as La_2O_3 . Corresponding values can also be readily determined by workers skilled in the art for other doping substances, such as niobium (Nb), bismuth (Bi), neodymium (Nd), cerium (Ce), samarium (Sm), tantalum (Ta) and other rare earths or similar materials.

Heretofore known ceramic dielectric capacitor bodies contained copper (Cu) in quantities ranging from 0.01 percent to 0.05 percent by weight calculated as CuO in relation to the total weight of the body or iron (Fe) in quantities ranging from 0.01 percent to 0.03 percent by weight, calculated as Fe_2O_3 in relation to the total weight of the body. However, even these types of capacitor bodies, at room temperatures, exhibited relatively low DK-values ranging from $20 \cdot 10^3$ to $50 \cdot 10^3$. Nevertheless, it appeared that the DK-values were extremely dependent on the voltage, since the individual crystallites had a conductive core and the application of voltage to the capacitor body at the outer electrodes appeared to only substantially decrease the crystal boundaries and allow a considerable field intensity to occur at such boundaries. Further, there is a substantially appreciable voltage dependency far below the Curie temperature or point (for example, at a Curie temperature of $120^\circ C.$).

An important feature of the invention is to provide a dielectric capacitor body consisting of a plurality of crystallites (polycrystalline bound together in a disc-shaped, tube-shaped or foiled-shaped ceramic body composed of barium-titanate material having a perovskite structure of the general formula:



wherein M^{II} is selected from the group consisting essentially of Ca, Sr, Pb, Mg and mixtures thereof; M^{IV} is selected from the group consisting essentially of Zr, Sn, and mixtures thereof; x and y are numerals ranging from 0 to 1, i.e. ranging up to one, and z is a numeral ranging from 1.005 to 1.05. This barium-titanate material is provided with at least two different doping substances, one of which predominantly effects N-conductivity on the interior of the crystallites and is selected from the grouping consisting of antimony (Sb), lanthanum (La), niobium (Nb), bismuth (Bi), cerium (Ce), neodymium (Nd), praseodymium (Pr), samarium (Sm) and tantalum (Ta) and the other of which predominantly effects P-conductivity at the surface layer of the crystallites and is selected from the group consisting of copper (Cu), iron (Fe), and manganese (Mn).

Another feature of the invention is to provide a polycrystalline (i.e., a plurality of bonded together crystallites) dielectric capacitor body wherein a plurality of insulating barrier layers are substantially uniformly distributed on the inside of the body and such layers are connected in series. Consequently, these insulating barrier layers provide a plurality of PN-transistions (i.e., PN-junctions) poled in blocking or passing directions.

Accordingly, it is an important object of the invention to increase the insulating stability and to lower the voltage dependence of the DK-value of a dielectric capacitor body in accordance with its application.

Another object of the invention is to provide a dielectric capacitor body and a method of making the same having inner barrier layers and a low temperature dependence.

It is another object of the invention to provide a dielectric capacitor body having barrier layers located at the surface of the crystallites comprising such body.

It is yet a further object of the invention to provide a dielectric capacitor body having inner barrier layers that have substantially no visible thickness.

Other objects, advantages and features of the invention will become more apparent with the teachings of the principles of the invention in connection with the disclosure of the preferred embodiments thereof in the specification, claims and drawings in which:

FIG. 1 is a prospective elevational view, with parts broken away, illustrating a disc-shaped capacitor body constructed in accordance with the principles of the invention;

FIG. 2 is an elevated sectional view, with parts broken away, of a tubular-shaped capacitor constructed in accordance with the principles of the invention;

FIG. 3 is an elevational sectional view, with parts broken away, of a stack capacitor body constructed in accordance with the principles of the invention;

FIG. 4 is a sectional fragmentary enlargement taken substantially at the encircled portion designated IV in FIGS. 1-3;

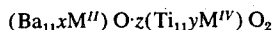
FIG. 5 is a graphical illustration of the DK-value of capacitors of the invention as a function of temperature for different sintering conditions;

FIG. 6 is a graphical illustration of the loss factor of the capacitors of the invention as a function of temperature for different sintering conditions; and

FIGS. 7 and 8 are graphical illustrations of the DK-value and the tangent of the loss angle δ as a function of temperature for capacitors of the present invention as a function of sintering temperature.

Before proceeding with a detailed description of the drawings, the composition of the barium-titanate crystallite having the perovskite lattice will be further described. As in-

dictated hereinbefore, the dielectric capacitor bodies of the invention are composed of a plurality of bonded crystallites in a ceramic form. The crystallites are composed of barium-titanate materials having a perovskite structure or lattice with a general formula of:



wherein M^{II} is a material selected from the group consisting of Ca, Sr, Pb, Mg, and mixtures thereof; M^{IV} is a material selected from the group consisting of Zr, Sn, and mixtures thereof; x and y are numerals ranging up to one; and z is a numeral in the range of 1.005 to 1.05. In other words, the quantity of the quadrivalent perovskite forming ingredient is 0.5 to 5 mol. percent greater than the quantity of the bivalent perovskite forming ingredient. These barium-titanate crystallites contain at least two different doping substances, a first of which is selected from the group consisting essentially of Bi, Ce, La, Nb, Nd, Pr, Sb, Sm and Ta which tend to predominantly effect N-conductivity on the inside or interior of such crystallites; and the second of which is selected from the group consisting of Cu, Fe and Mn which tend to predominantly effect P-conductivity on the surface layer or outer peripheral portions of such crystallites.

In accordance with the principles of the invention, the above defined dielectric capacitors of the invention have an increased insulating stability and a relatively low (and variable) dependence on voltage for the DK-value thereof in accordance with their application. This is achieved by including the aforesaid first doping substance (which predominantly effects the N-conductivity) in amounts ranging from 1.5 to 2.5 percent greater than the maximum doping quantity necessary to achieve the maximum conductivity of crystallites containing such doping substances; and by including amounts of the aforesaid second doping substance (which predominantly effects the P-conductivity) in the range of 0.01 to 0.15 percent by weight thereof. The amount of the doping substances are calculated on the basis of their respective oxides.

The DK-values discussed hereinbefore and hereinafter in regard to both the known and the now disclosed capacitor bodies, are the values for the dielectric constant (DK) and are conventionally designated far above the ϵ -value (dielectric and are to the specified material. These DK-values are obtained by computing a dielectric constant (DK) through measurements of the capacity of such capacitors modified by the physical dimensions of the capacitor body. Thus, throughout the instant discussion reference to the DK will be understood to mean apparent DK as determined in the aforesaid manner.

Control of crystalline growth (a process known to workers skilled in the art) or the addition of tin (with a correspondingly simultaneous shift of Curie Point) are utilized to insure that the crystallites of the instant invention are of a medium size in the range of 20 to 300 μ and preferably in the range of 100 to 300 μ (millimicrons). Such medium sized crystals exhibit an exceptionally large DK-value, however, the voltage dependence of the DK thereof tends to increase. Nevertheless, dielectric capacitors formed in accordance with the principles of the instant invention from the aforesaid medium sized crystals have exceptional utility, (or applicability) for example, as dielectric amplifiers.

In accordance with the preferred crystallite structures for the material comprising the dielectric capacitor bodies of the invention, antimony (Sb) is utilized as the first doping substance (previously identified) effecting the N-conductivity in amounts ranging from 0.15 to 0.25 percent by weight calculated on the basis of Sb_2O_3 . Copper (Cu) is utilized as the preferred second doping substance (previously identified) effecting the P-conductivity in amounts ranging from 0.01 to 0.15 percent by weight calculated on the basis of CuO .

The advantages of the instant invention become more obvious by the recognition of the fact that as the insulation of the surface or peripheral layers of the crystallites increase, more

copper is forced into such peripheral layers of the crystal lattice. However, an apparent contradiction or difficulty prevented workers in the art from recognizing this fact, since an increase in the amount of copper above its known maximum doping proportion results in a noticeable drop of the DK-value and sometimes as low as the effective ϵ -values. This contradiction may now apparently be explained or attributed to the fact that an increase in the amount of copper, reduces the conductivity of the entire crystallite, i.e. clearly indicating that the copper must enter into the interior of such crystallites.

Quite unexpectedly, surprisingly and in contradistinction to the teachings and suggestions of workers skilled in the art (as illustrated by the aforesaid literature) in regard to the optimum quantities of doping substances thought necessary, it has now been discovered that by increasing the amount of one doping substance, an increase in the amount of the other doping substance, i.e. copper, is possible. Such an increase results not only in the attainment of a considerable increase in the apparent DK, and in a marked improvement of the dielectric strength. This phenomenon may apparently be explained by the fact that by increasing the amount of a doping substance effecting the N-conductivity, the doping substance effecting the P-conductivity, i.e. copper, is prevented from entering into the interior of the crystallites and thereby increasing the amount of the P-conductivity effecting doping substance, i.e. copper, in the surface or peripheral layers of the crystallites. Nevertheless, the interior of such crystallites remains sufficiently conductive and substantially improved insulating properties are attained at the crystallite surface.

Other factors tending to influence the ability to incorporate the N-conductivity effecting doping substances (i.e., Bi, Ce, La, Nb, Nd, Pr, Sb, Sm, Ta, etc.) as well as the ability to incorporate the P-conductivity effecting doping substances (i.e., Cu, Fe, Mn, etc.) is the presence of titanium oxides utilized in the production of the ceramic bodies and the type of raw material thereof. Thus, in order to achieve comparably high DK-values and comparably high dielectric strength in the dielectric capacitors of the invention, it is necessary to utilize about 1.5 times more of both of the doping substances if the titanium oxide is utilized in its anatase form rather than in its rutile form.

Curie temperatures of the materials utilized as the dielectric capacitors can be adjusted in a conventional manner. For example, in crystalline structures where strontium or calcium are utilized as the M^{II} metals and tin and zirconium are utilized as the M^{IV} metals in the aforesaid perovskite crystallite structure, these metals tend to individually and/or jointly function to shift the Curie temperature of the dielectric capacitor material toward a lower temperature. In contrast, the utilization of lead as a M^{II} metal in the aforesaid perovskite structure functions to increase the Curie temperatures to values above 120° C.

The ability to shift toward lower temperatures in accordance with the principles of the invention affords an added advantage of having the operating temperature range lie below the Curie temperature. For example, if the Curie temperature of a particular composition is -10° C. (such as by inclusion of 20 mol. percent of tin), such as for material having the formula $\text{BaO} \cdot z(\text{Ti}_{0.6}\text{Sn}_{0.4})\text{O}_2$ wherein z is a numeral ranging from 1.005 to 1.05, the operating temperature range lies from 0° C. to far in excess of 100° C. The dielectric capacitor bodies of the invention possess, particularly above the Curie temperature, a very high DK-value. Such high DK-values, because of the operating temperature is in the cubical range, simultaneously decrease the loss factor to a very low value and suppress a decrease of the DK-value for ferroelectric substances (achieved by the increased amount of P-conductivity effecting substances, i.e. Cu, Fe, Mn, etc.) in accordance with the Curie-Weiss law. Consequently, such dielectric capacitor materials have a relatively low temperature coefficient.

The crystallites utilized in the formation of the dielectric capacitor bodies of the invention are preferably formed by intermixing suitable quantities of, for example, BaCO_3 and TiO_2

(TiO_2 is generally derived from and utilized in its raw ore form, i.e. rutile, anatase, or mixtures thereof). As will be appreciated, other perovskite starting materials, such as $(\text{Ba Pb}) \text{TiO}_3$; (Ba Ca TiO_3) ; (Ba Sr TiO_3) ; Pb (Zr Ti) O_3 , etc. can also be utilized. The perovskite starting materials are then intermixed with an N-conductivity effecting doping substance, such as for example, Sb_2O_3 in amounts ranging from 0.15 to 0.25 percent by weight and with a P-conductivity effecting doping substance, such as for example, CuO in amounts ranging from 0.01 to 0.15 percent by weight. This mixture is then generally uniformly pulverized, as by grinding in a ball mill for about 18 hours while adding about 0.5 mols. of water per mol. of mixture, dried and reacted (a solid-state reaction) at about 950° to 1100°C . An important factor in the preparation of the dielectric capacitor crystallites is the uniform intimate mixture of the materials and the attainment of an excess of TiO_2 (preferably attained through the so-called wet-grinding process described). More generally, (and in other words) it is important to obtain an excess of about 0.5 to 5 mols. percent of the M^{IV} metals over the M^{IV} metals.

However, as will be appreciated, suitable barrier layer capacitor crystallites having substantially equivalent qualities to those previously described may also be attained by utilizing a so-called dry grinding (or mixing) process. The dry grinding process achieves uniformity of the materials but several excess mols. percent of TiO_2 must be added to the initial mixture.

After the completion of the reaction (the solid-state reaction referred to hereinabove), the reaction product is again thoroughly pulverized or ground, such as in a ball mill, with the addition of about 0.5 mols. of water (however, dry grinding is also suitable) per mol. of reaction product for approximately 18 hours to achieve a fine-sized uniform particle mixture. This mixture is then dried and combined, in conventional manner, with an organic binding agent, such as for example, polyvinyl alcohol. This mixture is then pressed or formed into desired shape or configuration. The shaped dielectric capacitor bodies are then subjected to a final sintering operation at about 1300° to 1400°C . The completed capacitor bodies (after being provided with appropriate electrodes annealed or evaporated thereon) exhibit the values specified in the tables set forth hereinafter in regard to the dielectric constant DK , the $\text{tg}\delta$ (dielectric loss angle) and the voltage strength.

As will be appreciated, an exceptional advantage of the invention consists in providing a material having an extremely large apparent DK -value in a form suitable for capacitor use. A capacitor formed from such materials results in the formation of thin nonconductive layers at the surfaces or peripheries of crystallites, which have a well conducting polycrystalline (a plurality of such crystals bonded together) ceramic body. This is, in contrast to the heretofore known barrier layer capacitors, a quasi-volume capacity wherein a high dielectric strength is achieved (up to 100 v./mm. in certain cases). Further, an additional advantage coupled therewith is that the new capacitor material allows the production of capacitor bodies having extremely small (smallest of all known capacitors) geometric dimensions. This factor is extremely important in current microtechnique applications. For example, in utilizing the material of the invention having a DK of 10^5 (such as one having its Curie point shifted to a low temperature) can be formed into a capacitor body having, for example, 500 pf. and a dielectric strength of 200 v. (direct voltage) while having a diameter of about 0.3 mm. and a thickness of about 0.2 mm.

Further, the capacitor material of the invention offers a considerable manufacturing and technology advantages in comparison to the heretofore known barrier layer capacitor technology. One of the foremost of such advantages resides in the fact that, for example, the metal oxides necessary for the production of conductive BaTiO_3 crystalline particles, such as Sb_2O_3 and the metal oxides necessary for the production of the insulating intermediate or surface layers, such as CuO can be added directly to the perovskite-starting material (for example, suitable quantities of BaCO_3 and TiO_2) during the initial stage of the formation process.

As a result, it is feasible to utilize a starting or raw material for the production of commercial capacitors in a predetermined procedure or program. Accordingly, individual capacitor values can (as in the case of conventional capacitors) be readily attained through appropriate body shaping without the necessity of having to produce barrier layers on the finished ceramic body through various complicated processes.

Essentially, the material of the invention allows the production of so-called stacking or multilayer capacitors by, for example, applying spraying techniques (or other suitable techniques) to alternately spray thin ceramic layers (composed of, for example, converted BaTiO_3 powder with the appropriate metal oxide doping substances added thereto, such as the previously disclosed CuO and Sb_2O_3 in a suitable liquid or viscous form) on top of one another and subjecting such a stack to a sintering operation to form a parallelly connected electrical barrier layer capacitor body.

Referring now to the drawings, FIG. 1 generally illustrates a disc-shaped capacitor body 11 which functions as a dielectric and is produced from the novel material of the invention. Capacitor coats 12 and 13 are suitably fastened to this material and are provided with suitably fastened external connection means 14 and 15.

FIG. 2 illustrates a tubular-shaped ceramic body 21. Ceramic body 21 functions as a tubular capacitor and is provided with coatings 22 and 23. Outer current connection means 24 and 25 are suitably fastened to the coatings 22 and 23 respectively.

FIG. 3 illustrates a monolithic body 31 which is formed from a layer of ceramic materials of the invention stacked on top of one another in a manner conventional to the formation of ceramic bodies. The monolithic block 31 is divided by metallic layers 32 and 33 which function as condenser coatings. Layers 32 and 33 are alternatively led to the two connecting sides. Metal coatings 34 and 35 respectively, connect layers 32 and 33 with one another. As will be appreciated, outer connections (not shown) are attached to these outer metal coatings 34 and 35 for connection in a particular circuit.

FIG. 4 illustrates a considerably enlarged segment IV out of the ceramic bodies illustrated at FIGS. 1-3. The interior 41 of the crystallites have good N-conductivity characteristics. The surface of the peripheral layers 42 are located in surrounding relationship to the interior 41 of the crystallites and have good P-conductivity characteristics.

The tables set forth hereinafter more clearly illustrate the superior characteristics of the materials of the invention.

In the divisions of tables I through IV are all substantially identical. The first column enumerates the particular test in sequential order. The second column identifies the form of titanium oxide utilized in the formation of barium-titanate. Columns 3 and 4 specify the amounts of the indicated doping substance utilized. The last three columns indicate the electrical qualities of the particular material. The values given are average values attained from measuring 40 bodies in the respective tests. The DK -values specified in brackets below the average DK -values represent the highest measured value attained with the highest CuO quantity specified in column 4 for the respective tests. The CuO -quantity for the individual tests was varied within the two specified limits. The last column includes a notation "partially conductive" to indicate that these particular materials represent a good dielectric capacitor only to a limited extent.

A study of the data in tables I through IV will reveal that for every quantity of doping antimony, a quantity increase of doping copper results in an increase of the specific resistance to an extremely high value so that such dielectric capacitors possess exceptionally high dielectric strength. Simultaneously with the increase of the doping substances, i.e. copper and antimony, (although other specified N-conductivity effecting and P-conductivity effecting doping substance could also be utilized), the value for the tangent of the loss angle decreases, i.e. the loss angle improves. On the other hand, under the same conditions (i.e. increasing the doping substances), the

DK decreases with the copper additions thereby indicating that the insulating layer becomes thicker at the surface of the crystallites (although such thicker insulating layers are not visibly detectable). This tendency continues until too much doping antimony is present and a normal dielectric capacitor is formed, such as for the materials of tests 8 and 25. Test

material 21 indicates that when the amount or quantity of doping antimony reaches 0.175 percent by weight, the amount of copper is 0.05 to 0.06 percent by weight and is so large that a normal dielectric capacitor is formed, i.e. the individual crystallites do not have a conductive core or center with an insulating shell but rather insulating throughout.

TABLE I
[Material: BaTiO₃, doped with antimony and copper; T_c~120° C.]

Test Number	TiO ₂ -Starting substance for the formation of the BaTiO ₃	Doping substance		Electric qualities measured at 20° C.		
		Sb ₂ O ₃ , percent by weight	CuO, percent by weight	DK (in accordance with the given definition)	tg δ, 10 ³ , percent	Specific resistance ρ (Ohm cm.) Measuring voltage=320 v./mm.
1	Anatase	0.1	0.040-0.050	15,000	85	0.2-10 ⁸ , partially conductive.
2	do	0.1	0.055	12,000	80	Max. 4-10 ⁸ (at 20 v./mm.).
3	do	0.15	0.02-0.035	34,000	60	Max. 8-10 ⁸ , partially conductive.
4	do	0.15	0.04-0.08	28,000	40	Max. 60-10 ⁸ .
5	do	0.175	0.025-0.035	43,000 (60,000)	62	40-10 ⁸ , partially conductive.
6	do	0.175	0.04-0.05	46,000 (75,000)	50	160-10 ⁸ .
7	do	0.2	0.045-0.07	32,000 (55,000)	54	80-10 ⁸ .
8	do	0.25	0.045-0.07	2,000		Like normal capacitor

TABLE II
[Material: BaTiO₃, doped with antimony and copper; T_c~120° C.]

Test Number	TiO ₂ -Starting substance for the formation of the BaTiO ₃	Doping substance		Electric qualities measured at 20° C.		
		Sb ₂ O ₃ , percent by weight	CuO, percent by weight	DK (in accordance with the given definition)	tg δ, 10 ³ , percent	Specific resistance ρ (Ohm cm.) Measuring voltage=320 v./mm.
9	Rutile	0.1	0.008	2,000	100	4-10 ⁸ (at 20 v./mm.) partially conductive.
10	do	0.1	0.011	25,000	120	Max. 3-10 ⁸ .
11	do	0.1	0.013	20,000	100	Max. 7-10 ⁸ .
12	do	0.1	0.020	15,000	55	Max. 30-10 ⁸ .
13	do	0.125	0.010-0.013	35,500	70	Max. 1-10 ⁸ , partially conductive.
14	do	0.125	0.014-0.02	29,000	60	Max. 3.5-10 ⁸ .
15	do	0.125	0.025-0.030	14,000	50	Max. 30-10 ⁸ .
16	do	0.15	0.015-0.02	40,000	80	Max. 1.2-10 ⁸ , partially conductive.
17	do	0.15	0.022-0.030	40,000	40	Max. 15-10 ⁸ .
18	do	0.15	0.035-0.05	30,000	30	Max. 30-10 ⁸ .
19	do	0.175	0.01-0.022	47,000 (70,000)	72	Partially conductive.
20	do	0.175	0.025-0.045	31,000 (60,000)	47	170-10 ⁸ .
21	do	0.175	0.05-0.06	3,000		Partially like normal capacitors
22	do	0.20	0.005-0.02	4,700	62	9-10 ⁸ .
23	do	0.20	0.035-0.05	30,000 (40,000)	46	140-10 ⁸ .
24	do	0.225	0.035-0.075	28,000 (50,000)	34	240-10 ⁸ .
25	do	0.25	0.035-0.75	3,000		Like normal capacitors

TABLE III
[Material: BaO.2(Ti_{0.74}Sn_{0.26})O₂, doped with antimony and copper; T_c=40° C.]

Test Number	TiO ₂ -Starting substance for the formation of the BaTiO ₃	Doping substance		Electric qualities, measured at 20° C.		
		Sb ₂ O ₃ , percent by weight	CuO, percent by weight	DK (in accordance with the given definition)	tg δ, 10 ³ , percent	Specific resistance ρ (Ohm cm.)
26	Anatase	0.1	0.02-0.05	34,000 (75,000)	48	100-10 ⁸ (10 v./mm.), 10-10 ⁸ (200 v./mm.).
27	do	0.1	0.055-0.085	17,000 (32,000)	54	300-10 ⁸ (10 v./mm.), 100-10 ⁸ (300 v./mm.).
28	do	0.15	0.01			Conductive, no capacitor dielectric properties
29	do	0.15	0.013-0.025	36,000 (60,000)	65	1-10 ⁸ (10 v./mm.) partially conductive.
30	do	0.15	0.03-0.05	41,000 (55,000)	43	20-10 ⁸ (10 v./mm.), 2.8-10 ⁸ (100 v./mm.).
31	do	0.15	0.055-0.08	20,000 (35,000)	75	100-10 ⁸ (10 v./mm.), 20-10 ⁸ (100 v./mm.).
32	do	0.175	0.01-0.013	63,000 (65,000)	65	Partially conductive.
33	do	0.175	0.015-0.11	34,000 (62,000)	55	50-10 ⁸ (10 v./mm.), 9-10 ⁸ (200 v./mm.).
34	Rutile	0.15	0.01-0.015	50,000 (87,000)	53	2-10 ⁸ (10 v./mm.) partially conductive.
35	do	0.15	0.02-0.035	26,000 (60,000)	40	20-10 ⁸ (10 v./mm.), 3-10 ⁸ (100 v./mm.).
36	do	0.15	0.04-0.055	77,000 (115,000)	50	45-10 ⁸ (10 v./mm.), 4-10 ⁸ (150 v./mm.).
37	do	0.15	0.06-0.075	48,000 (95,000)	50	100-10 ⁸ (10 v./mm.), 12-10 ⁸ (200 v./mm.).
38	do	0.15	0.08-0.10	41,000 (60,000)	90	400-10 ⁸ (10 v./mm.), 370-10 ⁸ (150 v./mm.).
39	do	0.175	0.01-0.13	78,000 (80,000)	65	(0.5-20)-10 ⁸ (10 v./mm.) partially conductive.
40	do	0.175	0.015-0.06	66,000 (131,000)	65	100-10 ⁸ (10 v./mm.), 5-10 ⁸ (150 v./mm.).
41	do	0.175	0.065-0.1	49,000 (85,000)	80	500-10 ⁸ (10 v./mm.), 55-10 ⁸ (100 v./mm.).

TABLE IV

[Material: $\text{BaO} \cdot z(\text{Ti}_{0.6}\text{Sn}_{0.4})\text{O}_2$, doped with antimony and copper; $T_s = -10^\circ \text{C.}$]

Test Number	TiO ₂ -Starting substance for the formation of BaTiO ₃	Doping quantity		Average values from 40 measurements; electric qualities, measured at 20° C.		
		Sb ₂ O ₃ , percent by weight	CuO, percent by weight	DK (in accordance with the given definition)	tg δ · 10 ³ , percent	Specific resistance ρ (Ohm cm.)
42.....	Anatase...	0.1	0.01	50,000 (80,000)	60	Partially conductive 100·10 ⁸ (10 v./mm.).
43.....	do.....	0.1	0.013-0.055	42,000 (90,000)	95	100·1.8 (10 v./mm.), 3·10 ⁸ (100 v./mm.).
44.....	do.....	0.1	0.06-0.085	19,000 (46,000)	120	200·10 ⁸ (10 v./mm.), 80·10 ⁸ (200 v./mm.).
45.....	do.....	0.15	0.01-0.045	24,000 (58,000)	50	400·10 ⁸ (10 v./mm.), 4·10 ⁸ (150 v./mm.).
46.....	do.....	0.15	0.05-0.065	68,000 (115,000)	65	80·10 ⁸ (10 v./mm.), 5·10 ⁸ (100 v./mm.).
47.....	do.....	0.15	0.07-0.075	46,000 (90,000)	52	150·10 ⁸ (10 v./mm.), 8·10 ⁸ (50 v./mm.).
48.....	do.....	0.175	0.10-0.02	33,000 (55,000)	50	Partially conductive.
49.....	do.....	0.175	0.025-0.08	42,000 (82,000)	33	100·10 ⁸ (10 v./mm.), 45·10 ⁸ (100 v./mm.), 6·10 ⁸ (200 v./mm.).
50.....	Rutile.....	0.15	0.10-0.1	70,000 (130,000)	70	45·10 ⁸ (10 v./mm.), 1.5·10 ⁸ (50 v./mm.).
51.....	do.....	0.175	0.10-0.06	11,000 (60,000)	30	15·10 ⁸ (10 v./mm.).
52.....	do.....	0.175	0.065-0.1	68,000 (120,000)	75	100·10 ⁸ (10 v./mm.), 12·10 ⁸ (100 v./mm.).

In addition to the various advantageous control features previously discussed to modify the characteristics of the materials of the invention the graphs of FIGS. 5, 6 and 7 illustrate that the sintering conditions which such materials are subjected to are also a valuable means of controlling or modifying at least certain characteristics of such materials.

The graph illustrated at FIG. 5 shows the DK as a function of the temperature at different sintering conditions. The abscissa specifies the temperature in degrees centigrade while the ordinate specifies the DK (in accordance with the definition given hereinbefore). The material utilized is that of test 6 (identified in the above tables) and is a barium-titanate material (utilizing anatase as the raw material for titanium oxide) having 0.175 percent Sb₂O₃ and 0.04 percent CuO as the doping substances therein. The measuring frequency was 1 kHz. Curve 1 represents the DK of this material after it was sintered at 1350° C. for 30 minutes. Curve 2 represents the DK of the material after it was subjected to sintering temperature at 1350° C. for after hour. Curve 3 represents the DK of the material after it was sintered at 1360° C. for 2 hours.

The graph illustrated at FIG. 6 shows the loss factor as a function of the temperature at different sintering conditions. The material tested, the measuring frequency, the sintering temperatures and times are substantially identical to those explained in conjunction with FIG. 5 and, therefore, the reference numerals on the curves are the same as those utilized in FIG. 5.

The graph illustrated at FIG. 7 shows the DK and the tangent of the loss angle δ on the ordinate as a function of the temperature in degrees centigrade on the abscissa. The material utilized was that of test 50 (identified in the above tables), and has the empirical formula of $\text{BaO} \cdot z(\text{Ti}_{0.6}\text{Sn}_{0.4})\text{O}_2$ containing 0.15 percent by weight of Sb₂O₃ and 0.03 percent by weight of CuO as the doping substances. The measuring frequency was again 1 kHz. Curve 5 represents the DK trend of the material after it was sintered at 1360° C. for 2 hours. In contrast to this, curve 6 represents the DK trend of the material after it was sintered at 1350° C. for 1 hour. Curve 7 illustrates the trend of the tangent of the loss angle for the material after it was sintered at 1360° C. for 2 hours and curve 8 illustrates the trend of the tangent of the loss angle for the material sintered at 1350° C. for 1 hour.

The graph illustrated in FIG. 8 also shows the DK and the tangent of the loss angle δ on the ordinate as a function of temperature in degrees centigrade on the abscissa. The material utilized corresponds to the material of test 46 (identified in the above tables) and has an empirical formula of $\text{BaO} \cdot z(\text{Ti}_{0.6}\text{Sn}_{0.4})\text{O}_2$ containing 0.15 percent by weight of Sb₂O₃ and 0.06 percent by weight of CuO. The material was subjected to sintering conditions at 1360° C. for 2 hours. Curve 9 illustrates the trend of the DK and curve 10 illustrates the trend of the tangent of the loss angle.

Upon study of the specific resistance (Ohm·cm.) of the materials utilized for the graph data in FIGS. 5-8 it will be seen that the material of test 6 (identified in the above tables) has a specific resistance of 160·10⁸ (at 320 v./mm.); the

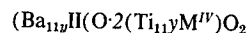
material of test 46 (also identified in the tables) has a specific resistance of 80·10⁸ (at 10 v./mm.) or 5·10⁸ (at 100 v./mm.); and that the material of test 50 (identified in the above tables) has a specific resistance of 45·10⁸ (at 10 v./mm.) or 1.5·10⁸ (at 50 v./mm.). It is therefore apparent that such materials must, necessarily, have a tremendous amount of dielectric strength. Consequently, it will be appreciated that through the principle of the invention an excellent material for barrier layer capacitors is provided which, with the shifting of the Curie temperature toward temperatures below the operating temperature of a particular utility, has a very small and insignificant temperature dependence of the DK.

It will thus be seen that we have provided a novel dielectric capacitor composed of a barium-titanate perovskite material containing at least two different doping substances which meet all of the aforesaid objects.

It will be understood that modifications and variations may be effected on the preferred embodiments disclosed without departing from the spirit and scope of the present invention.

We claim:

1. A dielectric capacitor body composed of a plurality of joined together crystallites to form a ceramic body, said crystallites being composed of a barium-titanate material having a perovskite structure of the formula:



wherein M^{IV} is a material selected from the group consisting essentially of Ca, Sr, Pb, Mg, and mixtures thereof; M^{IV} is a material selected from the group consisting essentially of Zr, Sn and mixtures thereof; x and y are numerals ranging up to one; and z is a numeral ranging from 1.005 to 1.05; said barium-titanate material including at least a first and a second doping substance, said first doping substance predominantly producing N-conductivity in the inside of said crystallites and said second doping substance predominantly producing P-conductivity in the surface layers of said crystallites, said first doping substance being present in amounts ranging from 1.5 to 2.5 times greater than the maximum quantity of the substance necessary for producing maximum conductivity in said barium-titanate material and said second doping substance being present in amounts ranging from 0.01 to 0.15 percent by weight determined on the basis of its oxide.

2. The dielectric capacitor as defined in claim 1 wherein the first doping substance is a material selected from the group consisting essentially of Bi, Ce, La, Nb, Nd, Sb, Sm and Ta and the second doping substance is a material selected from the group consisting essentially of Cu, Fe, and Mn.

3. The dielectric capacitor as defined in claim 1, wherein the first doping substance is present in amounts ranging from 0.15 to 0.25 percent by weight, the amount of said first doping substance being calculated on the basis of its oxide.

4. The dielectric capacitor as defined in claim 3, wherein the first doping substance is antimony and the amount thereof is calculated on the basis of Sb₂O₃.

5. The dielectric capacitor as defined in claim 1, wherein the second doping substance is copper and the amount thereof is calculated on the basis of CuO.

6. The dielectric capacitor body as defined in claim 1 wherein the quantity of the quadrivalent perovskite materials is present in amounts ranging from 0.5 to 5 mol. percent greater than the quantity of the bivalent perovskite materials.

7. The dielectric capacitor body as defined in claim 1, wherein the specific resistance of said dielectric capacitor body ranges from about $1.5 \cdot 10^8$ to about $500 \cdot 10^8$ ohms at 10 v./mm. to 320 v./mm.

8. The dielectric capacitor body as defined in claim 1, wherein the dielectric constant-value of said dielectric capacitor body ranges from about 10^8 to $1.3 \cdot 10^8$.

9. The dielectric capacitor body as defined in claim 1 wherein the quantity of TiO_2 is present in amounts ranging from 0.5 to 5 mol. percent greater than the quantity of the bivalent perovskite materials.

10. The dielectric capacitor body as defined in claim 1 wherein the quantity of TiO_2 is present in amounts ranging from 0.5 to 5 mol. percent greater than the quantity of BaO.

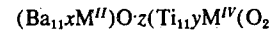
11. A dielectric capacitor body composed of a polycrystalline ceramic body the crystallites composing said body consisting essentially of a barium-titanate perovskite material having the formula:



wherein z is a numeral ranging from 1.005 to 1.05, said barium-titanate material including about 0.15 percent to 0.25 percent by weight Sb_2O_3 predominantly producing N-conductivity in the inside of said crystallites and about 0.01 to 0.15 percent by weight of CuO predominantly producing P-conductivity in the surface layers of said crystallites.

12. The method of producing a dielectric capacitor body comprising: (1) forming a barium-titanate crystallite having a

perovskite structure of the formula:



wherein M^{II} is selected from the group consisting essentially of Ca, Sr, Pb, Mg and mixtures thereof; M^{IV} is selected from the group consisting essentially of Zr, Sn and mixtures thereof; x and y are numerals ranging up to one, and z is a numeral ranging from 1.005 to 1.05; (2) admixing at least a first and a second doping substance to said crystallites to achieve a substantially uniform intimate mixture thereof, said first doping substance predominantly producing N-conductivity in the inside of the crystallites, said second doping substance predominantly producing P-conductivity in the surface layers of said crystallites; (3) heating said mixture to a temperature in the range of 950°C. to 1100°C. to achieve a solid-state body reaction thereof; (4) uniformly pulverizing the reacted mixture; (5) mixing an organic binder with such pulverized mixture; and (6) forming a capacitor body thereof and subjecting said body to sintering conditions at temperatures in the range of 1300°C. to 1400°C. for a period of time ranging from about 30 to 150 minutes.

13. The method as defined in claim 12, wherein the step (1) comprises uniformly intermixing an amount of BaCO_3 and an amount of TiO_2 , in excess of the aforesaid BaCO_3 amount, said excess amount being in the range of 0.5 to 5 mol. percent.

14. The method as defined in claim 13, wherein the first doping substance is a material selected from the group consisting essentially of Bi, Ce, La, Nb, Nd, Pr, Sb, Sm and Ta and the second doping substance is a material selected from the group consisting essentially of Cu, Fe, and Mn.

15. The method as defined in claim 14, wherein the first and second doping substances are in their respective oxide forms.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,569,802 Dated March 9, 1971

Inventor(s) Horst Brauer and Renate Kuschke PAGE - 1

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 5, "pervoskite" should read--perovskite--;

line 6, " $(\text{Ba}_{1-x}\text{M}^{\text{II}})\text{O}\cdot\text{z}(\text{Ti}_{1-y}\text{M}^{\text{IV}})\text{O}_2$ " should read--
 $(\text{Ba}_{1-x}\text{M}^{\text{II}}_x)\text{O}\cdot\text{z}(\text{Ti}_{1-y}\text{M}^{\text{IV}}_y)\text{O}_2$ --;

line 10, " M^{II} II" should read-- M^{II} --.

Column 3, line 7, " $(\text{Ba}_{1-x}\text{M}^{\text{II}})\text{O}\cdot\text{z}(\text{Ti}_{1-y}\text{M}^{\text{IV}})\text{O}_2$ " should read
 $(\text{Ba}_{1-x}\text{M}^{\text{II}}_x)\text{O}\cdot\text{z}(\text{Ti}_{1-y}\text{M}^{\text{IV}}_y)\text{O}_2$ --;

line 45, cancel "and are" and insert therefore--consta
peculiar--.

Column 4, line 52, cancel "1a";

line 61, " $\text{BaO}\cdot\text{z}(\text{Ti}_{0.6}\text{Sn}_{p.4})\text{O}_2$ " should read-- $\text{BaO}\cdot\text{z}$
 $(\text{Ti}_{0.6}\text{Sn}_{0.4})\text{O}_2$ --.

Column 5, line 20, " m^{IV} " should read-- M^{IV} --.

Column 8, line 4, "si" should read--is--.

Column 9, TABLE IV, TEST NUMBER 43, column 5, " $100\cdot\text{L}$ "
should read-- $100\cdot 10^8$ --;

contd.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,569,802

Dated March 9, 1971

Inventor(s) Horst Brauer and Renate Kuschke

PAGE- 2

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

TEST NUMBER 48, column 3, "0.10-0.0" should read--0.01-0.02--;

TEST NUMBER 50, third column, "0.10" should read--0.01-0.1--.

Column 9, line 36, "at" should read--of--;

line 37, cancel "2 hours" and insert therefore--1 hour
Curve 4 represents the same material after sintering at 1360° C.
2 hours--;

line 69, "at" should read--of--.

Column 10, line 20, "80·10⁸" should read--80·10⁸--;

line 21, after "tables" insert--)--;

line 45, "(Ba_{11y}II (O·2 (Ti_{11y}M^{IV}) O₂" should read--(B
M^{II}_x) O·z (Ti_{1-y}M^{IV}_y) O₂--.

Column 11, line 10, "500·10⁸" should read--500·10⁸--.

Column 12, line 3, "Ba_{11x}M^{II}) O·z (Ti_{11y}M^{IV}) (O₂" should read
(Ba_{1-x}M_x^{II}) O·z (Ti_{1-y}M_y^{IV}) O₂--;

line 23, cancel "12, wherein".

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,569,802 Dated March 9, 1971

Inventor(s) Horst Brauer and Renate Kuschke PAGE - 3

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 53, "if" should read--is--;

line 66, " $20 \cdot 10^3$ " should read-- $20 \cdot 10^3$ --.

Column 3, lines 44-45, "(dielectric and are " should read--(dielectric constant) peculiar--;

line 56, "mp" should read-- μm --;

line 57, "m μ (millimicrons)" should read-- μm (microns)

Column 5, line 15, "initmate" should read--intimate--;

line 20, " m^{IV} " should read-- M^{IV} --.

Column 6, line 46, "condcutivity" should read--conductivity--.

Column 9, line 36, "after" should read--one--.

Signed and sealed this 18th day of January 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents