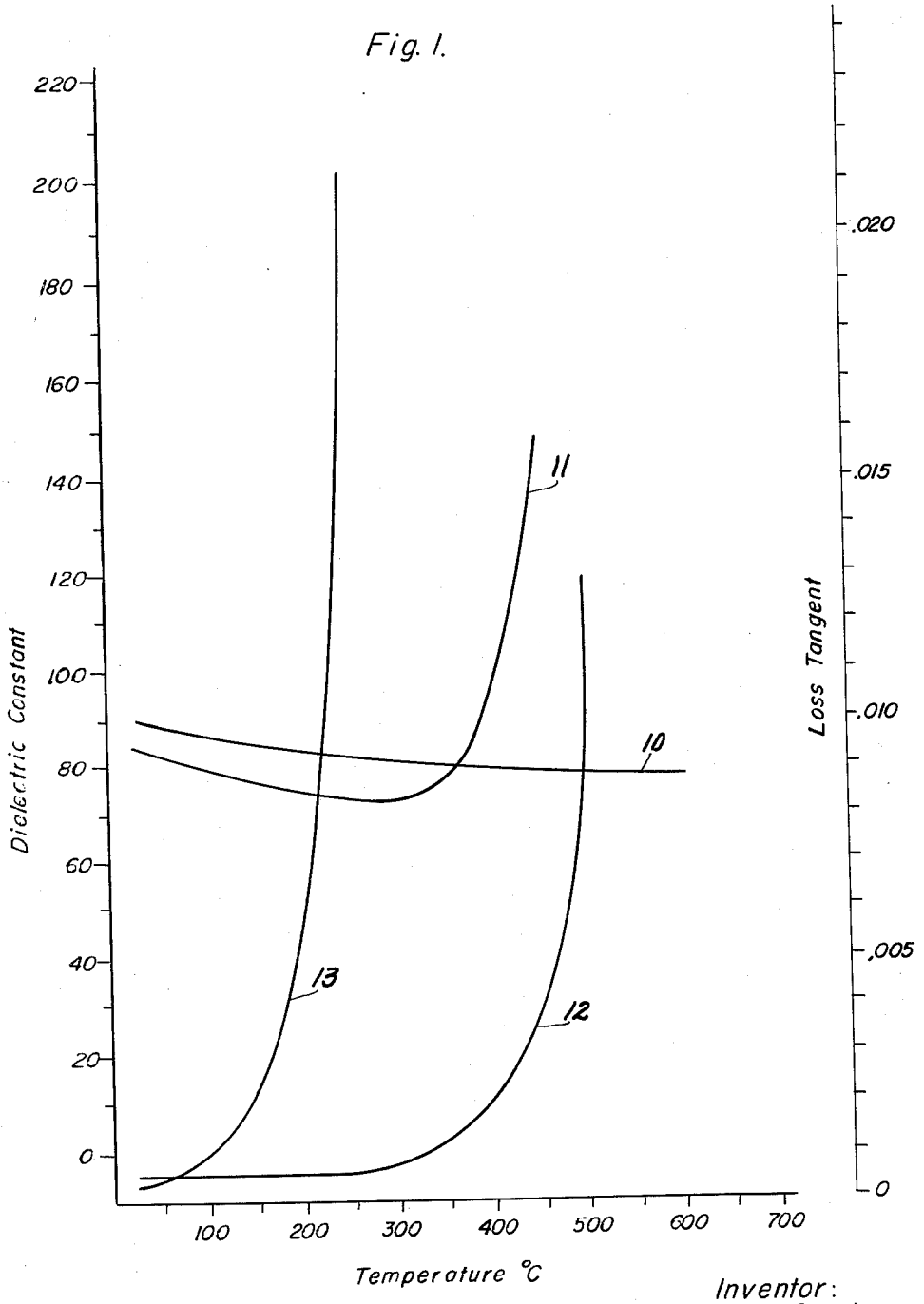
Oct. 3, 1961 G. GOODMAN 3,002,841

DIELECTRIC MATERIALS

Filed March 16, 1960 4 Sheets-Sheet 1

Fig. 1.



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DIELECTRIC MATERIALS

Filed March 16, 1960 4 Sheets-Sheet 2

Fig. 2.

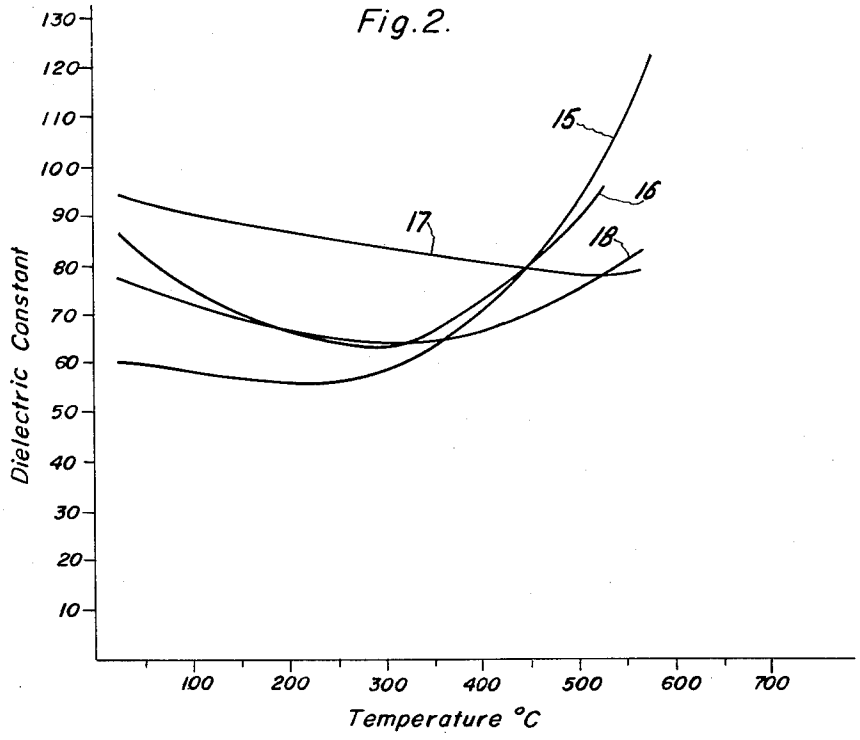
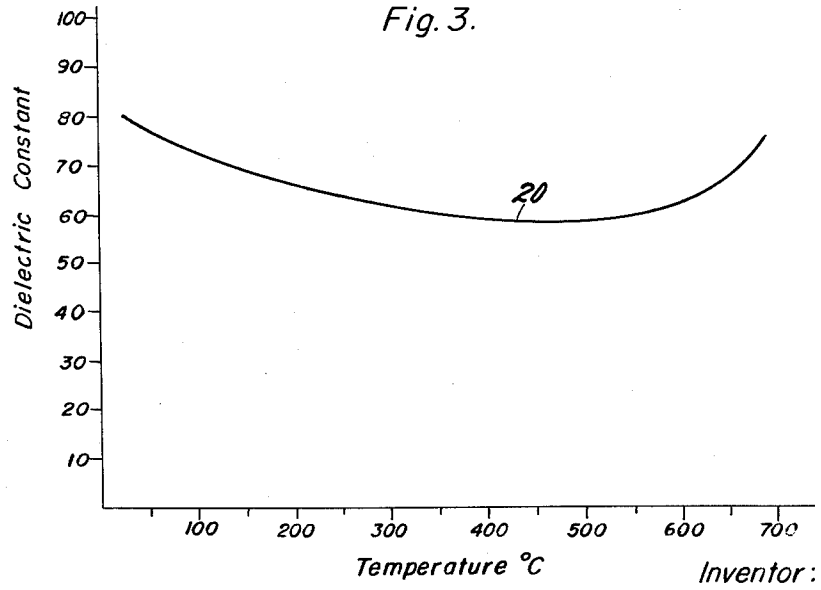


Fig. 3.



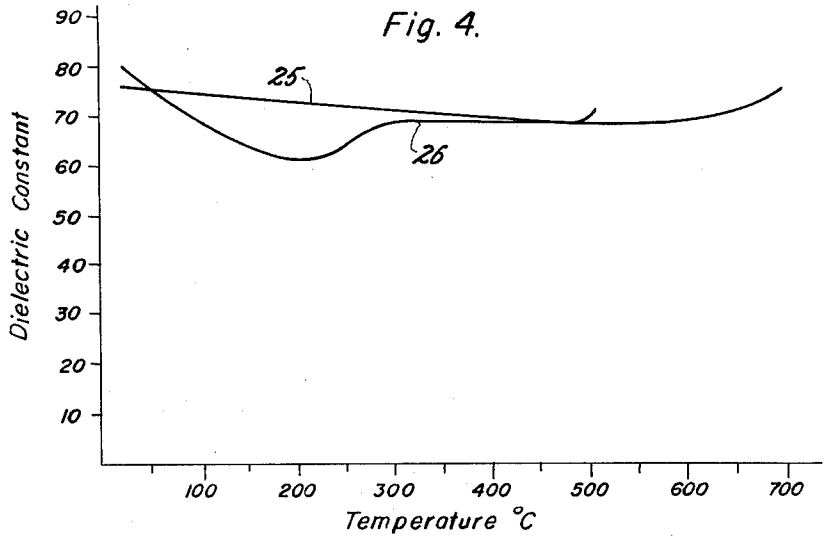
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DIELECTRIC MATERIALS

Filed March 16, 1960 4 Sheets-Sheet 3

Fig. 4.



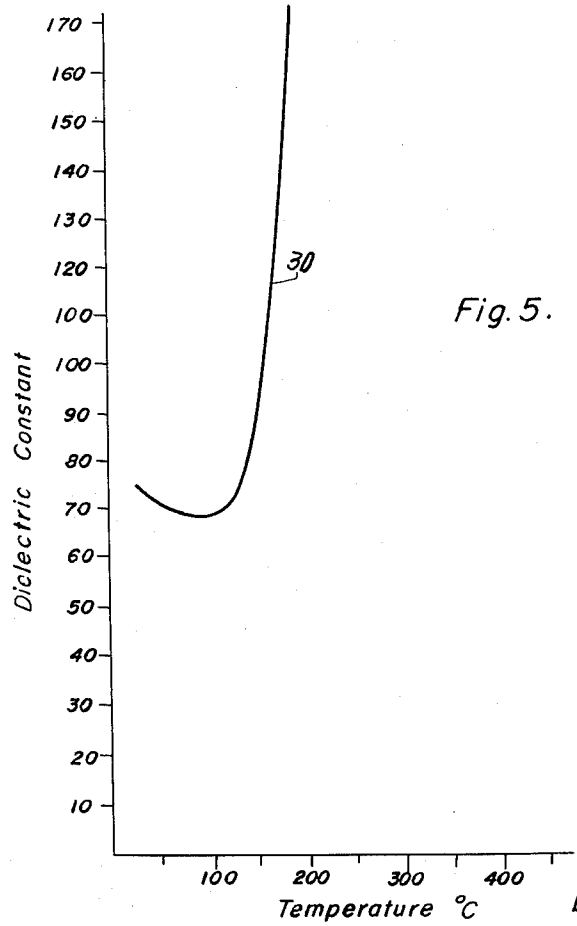


Fig. 5.

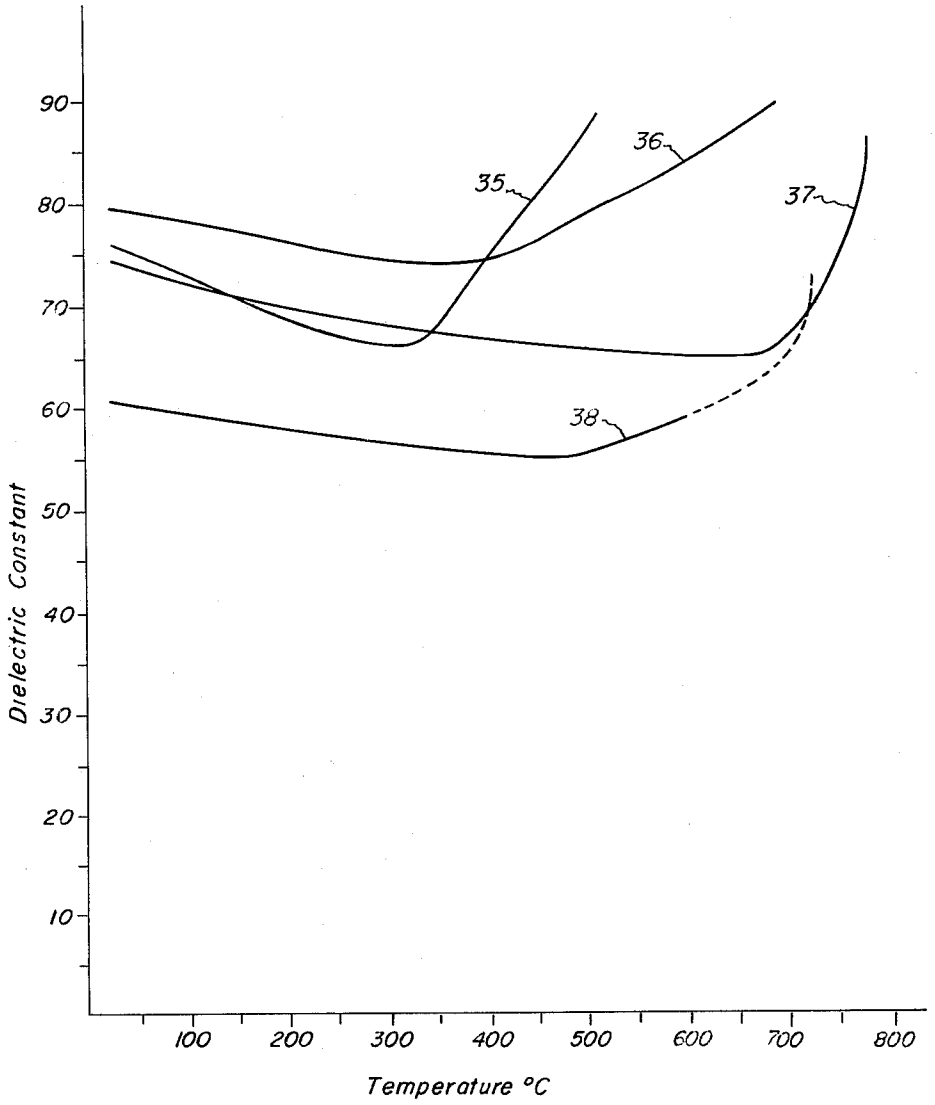
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DIELECTRIC MATERIALS

Filed March 16, 1960 4 Sheets-Sheet 4

Fig. 6.



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United States Patent Office 3,002,841 Patented Oct. 3, 1961

3,002,841

DIELECTRIC MATERIALS

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Filed Mar. 16, 1960, Ser. No. 15,500
11 Claims. (Cl. 106—39)

This invention relates to polycrystalline dielectric materials and, more particularly, to vitrified ceramic compositions having comparatively high substantially invariant dielectric constants up to about 350° C. and only slightly varying constants up to about 500° C.

This application is a continuation-in-part of copending application Serial No. 756,412, now abandoned, entitled "Dielectric Materials," filed August 21, 1958, and assigned to the same assignee as the present invention.

The increasing use of electrical and electronic equipment for various applications often requires development of apparatus having components capable of withstanding unusual and often severe operating conditions. One of the more commonly encountered difficulties is that of producing parts capable of withstanding comparatively high temperatures and capable of successfully performing their intended functions at such elevated temperatures, as well as at ordinary temperatures. Radio, radar, and analogous systems are examples of apparatus which many times must operate over a wide range of temperatures.

Dielectrics are commonly used in a number of electrical applications, the present invention being concerned primarily with polycrystalline ceramic dielectrics for use in capacitors and the like. Capacitor dielectrics can be divided into three general categories, depending on their dielectric constants and dielectric loss tangents.

The following Table I shows the general order of the dielectric properties of the three groups measured at 10^4 cps. and the stability of these properties over a comparatively wide temperature range, say 0° C. to 350° C.

Table I

Dielectric Material	Dielectric Constant	Loss Tangent	Temperature Stability
Vitreous Silica	4	.0001	Good.
TiO_2	100	.001	Fair to Poor.
$BaTiO_3$	1,000	.01	Poor.

The dielectrics of this invention fall generally within the class of dielectric materials having dielectric constants on the order of 100, that is, with titania and related materials. However, the temperature stability of the present dielectric materials is appreciably greater than not only those of the materials of moderate dielectric capacity but also those of higher and lower capacities.

It is a principal object of this invention to provide vitrified oxide compositions having relatively high dielectric constants and comparatively low loss tangents up to about 500° C.

An additional object of this invention is to provide ternary oxide compositions having dielectric constants which are substantially uniform at temperatures up to about 300° C. and which vary only slightly up to 500° C.

Other objects and advantages of this invention will be in part obvious and in part explained by reference to the accompanying drawings and specification.

In the drawings:

FIG. 1 shows typical curves of dielectric constants and dielectric loss tangents versus temperature measured at 10^4 cps. for the compositions of this invention as compared with corresponding curves for sintered titania;

FIG. 2 shows curves of dielectric constant versus temperature for various compositions of this invention;

FIG. 3 shows a curve similar to those of FIG. 2 for an additional composition;

FIG. 4 shows curves of dielectric constant versus temperature for still further compositions of the present invention;

FIG. 5 shows the effect of temperature on the dielectric constant of a binary composition of strontium and tantalum oxide, a known, vitrified ceramic dielectric; and

FIG. 6 shows the effect of temperature on the dielectric constants of materials produced according to this invention and in which the ratio of tantalum to the combined amounts of the other metals is varied.

Briefly, the present invention concerns the production of vitrified ceramic compositions having substantially invariant dielectric constants up to about 350° C., only slightly varying constants from 350–500° C., and also having suitably low loss tangents (tan δ). The compositions are made up of a vitrified combination of an alkaline earth such as barium oxide, strontium oxide, or calcium oxide and combinations thereof, an oxide of a metal from the group zirconium, titanium, tin, and combinations thereof, and tantalum oxide.

As previously mentioned, it is many times desirable to obtain dielectric compositions which have comparatively high dielectric constants, for example, on the order of 100, and relatively low loss tangents, for example, on the order of 0.0005.

While the required properties are approached by titania and other ceramics at room temperature, they are retained only over a very limited temperature range. The compositions of the present invention make it possible, however, to retain the desired properties virtually constant from room temperature to 350° C. and only slightly variant from 350–500° C.

The compositions are vitrified, polycrystalline ceramics for use in suitable apparatus such as the capacitors already discussed. Specifically, the compositions are preferably composed essentially of a vitrified combination of (*a*) an alkaline earth selected from the group consisting of barium oxide, strontium oxide, and combinations thereof in all proportions, although calcium oxide may also be used. The second component (*b*) of the composition is one of the metals, zirconium, titanium, or tin, or combinations thereof which are oxidized during subsequent processing, and the final component is (*c*) tantalum oxide.

It will be appreciated that the components of the system can be combined as metals and subsequently oxidized prior to vitrification. However, in most instances, it is preferred to add the materials either in the oxide state, since they are normally more readily and inexpensively obtainable in this state. They may also be added as oxygen-containing compounds, such as barium and strontium oxalates and/or carbonates. Obviously, early in the sintering process, the oxalate and the carbonate will break down to form the oxide of the metal, which becomes part of the final product.

Sample compositions made according to the present invention are:

$3SrO \cdot ZrO_2 \cdot 2Ta_2O_5$; $3BaO \cdot ZrO_2 \cdot 2Ta_2O_5$; and
$3SrO \cdot SnO_2 \cdot 2Ta_2O_5$; $3BaO \cdot TiO_2 \cdot 2Ta_2O_5$.

The following Table II lists the nominal weight percent compositions of sample polycrystalline bodies made according to the present invention:

Table II

No.	Ba-Oxalate	$SrCO_3$	Ta_2O_5	TiO_2	ZrO_2	SnO_2	Firing, Temp., ° C.
1	41.62		51.18		7.20		1,675
2	42.73		52.52	4.75			1,500
3	41.03		50.38			8.59	1,750
4		30.66	60.79		8.55		1,675
5		31.63	62.70	5.67			1,500
6		30.12	59.70			10.18	1,675

Polycrystalline ceramic dielectric bodies were made by mixing suitable quantities of the various selected components (see Table II) in a ball mill in amyl acetate for 5 to 10 hours. Alcohol can be used in place of amyl acetate if desired. Following the milling of the materials, they were dried and calcined in a platinum container at about 1350° C. The calcined material was crushed to —200 mesh, since it had agglomerated somewhat during firing, and carbowax was added to give consistency suitable for pressing the material into one inch diameter buttons, one-eighth inch thick. The buttons were then fired in air for 1 to 1½ hours on a platinum base at the temperatures indicated in Table II. Neither the temperature nor the time is critical, as the time at maximum temperature may vary as much as an hour and the maximum temperature as much as 25° C., for example.

The dielectric constants and loss tangents (tan δ) were measured for two of the preceding compositions over a temperature range of from 25 to 600° C. The first of these compositions was $3SrO \cdot ZrO_2 \cdot 2Ta_2O_5$ and the values obtained are shown in the following Table III:

Table III

Temperature, ° C.	10 kc./sec.	
	Dielectric Constant	Tan. δ
25	99	.0003
100	96	.0003
200	94	.0003
300	91	.0007
400	89	.0019
500	88	.0113
600	87	.084

The second composition differed from the first in that the zirconia component was replaced by tin oxide, so that the formula reads $3SrO \cdot SnO_2 \cdot 2Ta_2O_5$. The dielectric constants and loss tangents of this material, as functions of temperature, are shown in Table IV which follows:

Table IV

Temperature, ° C.	10 kc./sec.	
	Dielectric Constant	Tan. δ
25	76	.0007
100	75	.0007
200	73	.0007
300	72	.0009
400	72	.0029
500	70	.0140
600	69	.734

Comparing the values shown in Tables III and IV, it is obvious that the dielectric constant changes very little from room temperature up to the range of from 300 to 400° C. and that the variation to 500° C. is slight. In general, substantial invariancy occurs up to about 350° C., this fact being ascertainable by plotting the dielectric constant values against the temperature. The loss tangent increases very little up to about 300 to 400 C., although there is more of an increase from about 350 to 500° C. than occurs at the lower temperatures.

Referring to FIG. 1 the curves indicate the effect of temperature on the dielectric constants and loss tangents of the ternary combination, $3SrO \cdot ZrO_2 \cdot 2Ta_2O_5$ of the present invention, with similar curves for polycrystalline TiO_2 being shown for purpose of comparison. Specifically, curve **10** shows the dielectric constant of the ternary combination $3SrO \cdot ZrO_2 \cdot 2Ta_2O_5$ at temperatures up to about 600° C. Comparing curve **10** with the curve **11**, which shows the effect of temperature on titania (TiO_2) ceramic, it is obvious that the initial dielectric constant of the titania is slightly lower than that of the ternary dielectric and that it changes rapidly after a temperature of about 300° C. is exceeded. The dielectric constant of the ternary, however, remains substantially invariant up to the 600° C. figure shown in the drawing. Similarly, the loss tangent curves **12** and **13** for the ternary dielectric and the titania respectively show that the loss tangent for the titania begins to increase at a much lower temperature than is true for the material of the invention.

An important factor to be considered, in order that the ternary composition has optimum dielectric properties, is the molar ratio of the alkaline earth metal chosen to the metal selected from the group composed of zirconium, titanium, and combinations thereof. Generally, the alkaline earths and the zirconium, titanium and tin oxides should be present in such molar ratios in the vitrified product that there are from 1.25 to 1.75 mols of alkaline earth metal present for each 0.25 to 0.75 mol of zirconium, titanium or tin. Normally, the best ratio is 1.5 mols of the alkaline earth metal to 0.5 mol of either zirconium, titanium or tin, to achieve optimum results. That is, a ratio of 3 mols of alkaline earth metal to 1 mol of zirconium, titanium or tin is preferred, although it will be recognized that these figures are not absolute and compositional variations are possible. For example, 1.25 to 1.75 mols of alkaline earth metal to 0.5 mol of metal from group (*b*) results in formation of a good dielectric. While these molar ratios represent preferred amounts, other amounts can be used and still obtain a ceramic having desirable properties which are unattainable in most existing, polycrystalline dielectrics. Thus, if instead of 1.5 mols of strontium to 0.5 mol of zirconium, for example, there is 1 mol of strontium to 1 mol of zirconium, improved properties are still obtained.

The value of having the proper molar ratio between the metals of the alkaline earth group (*a*) and the metals from the zirconium, titanium, and tin group (*b*), can clearly be seen by referring to FIG. 2 of the drawings. In this graph, the dielectric constants of materials made with varying molar ratios between the metals of the (*a*) and (*b*) groups have been plotted against temperature. All measurements were made at 10 kilocycles per second.

Since we are at the moment concerned only with the molar ratios between the metals, the following discussion deals only with the metals and omits any reference to the oxides of the compounds which will normally be present in the finished material. Referring to curve **15** of FIG. 2, the ternary dielectric used contained equal amounts of strontium and zirconium with 2 mols of tantalum. Therefore, the molar ratio between the strontium and zirconium is 1 to 1 and the combined amounts of zirconium and strontium equals the total amount of tantalum, so that the molar ratio between these two materials is also 1 to 1. The curve **16** represents a change in the proportions between strontium and zirconium, there now being 1.75 mols of strontium to 0.25 mol zirconium. While the curve **16** does not vary as much as the curve **15** over the temperature range, it does vary more than the curve **17** in which 1.5 mols of

strontium are present to 0.5 mol zirconium. When the ratio drops still further to 1.25 mols of strontium to 0.75 mol of zirconium, the curve **18** once again begins to assume a concave configuration.

Comparison of curves **15** through **18** indicates that the optimum molar ratio is present when 1.50 mols of strontium or other alkaline earth metal to 0.5 mol of zirconium or tin or titanium, are present. Referring to FIG. 3, the curve **20** indicates the characteristics of the ceramic composition having the metals in the molar proportions: 1.5 Ba, 0.5 Sn, and 2.0 Ta. This curve varies moderately, compared with known dielectrics, throughout the entire temperature range tested.

FIGURE 4 shows the invariancy of the dielectric constants of the materials of the present invention. In this instance, the curve **25** shows the characteristics for compositions having metals in the molar proportions, 1.5 Sr, 0.5 Sn, and 2.0 Ta. It is obvious that while there are minor fluctuations in the capacitance values of this material, it remains substantially invariant throughout a wide temperature range. The material whose properties are indicated by the curve **26** has substantially the same dielectric properties as the material whose properties are shown by FIG. 25, with the exception that somewhat greater fluctuations were noted at intermediate temperatures. The metal composition of this material is 1.5 Sr, 0.5 Ti, and 2.0 Ta. The only composition change of the latter ceramic from the former is the substitution of titanium for tin.

FIG. 5 shows the importance of including one of the materials from the (*b*) group of zirconium, titanium, tin and combinations thereof. In this instance, the compound includes 2 mols of strontium and 2 mols of tantalum so that it is a binary composition. It is obvious that the dielectric properties, as indicated by curve **30**, change markedly at about 125° C. Thus, although the amount of the (*b*) group metal which is used is small, it is nevertheless an important element in attaining the desired dielectric properties.

It is understood, of course, that in the preceding examples the molar ratio of the total amounts of the two (*a*) and (*b*) group metals to the amount of tantalum is 1 to 1.

To obtain optimum dielectric and loss tangent properties, a definite molar relationship between the amount of tantalum metal present and the total amount of the two metals selected from the (*a*) and (*b*) groups should be present. Specifically, the total molar concentration of the (*a*) and (*b*) group metals should preferably range from about 0.75 to 1.50 mols for each mol of tantalum metal present in the oxide. Compositions in which there are from about 1.00 to 1.25 mols of the combined amounts of the metals from the (*a*) and (*b*) groups for each mol of tantalum represent the preferred compositions since slightly greater stability and better dielectric and loss tangent properties are obtained. Several compositions were prepared to test the effect of varying the ratio between the (*a*) and (*b*) group metals and the tantalum. These compositions are listed in the following Table V:

Table V

No.	Formula			Weight percent		
	SrO	ZrO_2	$2Ta_2O_5$	ZrO_2	Ta_2O_5	$SrCo_3$
1	2.250	0.750	2	7.10	67.54	25.36
2	2.625	0.875	2	7.86	64.07	28.06
3	3.375	1.125	2	9.17	58.11	32.72
4	3.750	1.250	2	9.73	55.53	34.74

Samples were prepared in the manner described earlier in the application and tested to determine their dielectric properties. Referring to FIG. 6 of the drawings, the curve **35** shows the dielectric properties of the first of the four compositions listed in Table V, while the three remaining curves **36, 37** and **38** illustrate the dielectric properties of the remaining three samples. Curve **35** clearly shows that the dielectric constant of a polycrystalline ceramic body produced according to this invention and having a ratio between the combined amounts of the (*a*) and (*b*) group metals and the (*c*) group metal tantalum of 0.75 to 1.00 will be substantially invariant at temperatures up to about 350° C. before conductivity begins to increase significantly. Similarly, curve **38** shows that the dielectric constant of a ceramic body having a ratio of about 1.25 to 1.00 between the combined amounts of the (*a*) and (*b*) group metals and the tantalum is substantially invariant to temperatures as high as 550° C. The other curves **36** and **37** represent compositions having intermediate ratios and these materials also have dielectric constants which remain substantially invariant to elevated temperatures. For the last two compositions in Table V, dielectric loss tangents of less than 10^{-4} were measured up to 200° C. For the second composition, this low level of dielectric loss persisted to 100° C.; and for the first composition, it was observed at room temperature. Upon heating, dielectric loss increased from these values in the usual manner.

Thus, the present invention makes possible the attainment of substantially invariant dielectric constants over a wide temperature range, all of the compositions showing substantial invariancy up to about 350° C. and only slight variance in the values to temperatures up to about 500° C., and occasionally even higher. The loss tangent values are also quite acceptable for most applications.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A ceramic dielectric composition having a dielectric constant varying only slightly up to about 500° C., said composition being composed essentially of a vitrified combination of ingredients composed essentially of (*a*) an alkaline earth selected from the group consisting of strontium oxide, barium oxide, calcium oxide, and mixtures thereof, (*b*) a metallic oxide selected from the class consisting of zirconium oxide, titanium oxide, tin oxide, and mixtures thereof, and (*c*) tantalum oxide, the metals of the oxides of (*a*) and (*b*) being present in such molar ratios that the total molar concentration of said metals ranges from 0.75 to 1.50 of the molar concentration of tantalum in said tantalum oxide.

2. A ceramic dielectric as defined in claim 1 wherein said alkaline earth is strontium oxide.

3. A ceramic dielectric as defined in claim 1 wherein said alkaline earth is barium oxide.

4. A ceramic dielectric as defined in claim 1 wherein said alkaline earth is a mixture of strontium and barium oxides.

5. A ceramic dielectric composition having a dielectric constant varying only slightly up to about 500° C., said composition being composed essentially of a vitrified combination of ingredients composed essentially of (*a*) an alkaline earth selected from the group consisting of strontium oxide, barium oxide, calcium oxide, and mixtures thereof, (*b*) a metallic oxide selected from the class consisting of zirconium oxide, titanium oxide, tin oxide, and mixtures thereof, and (*c*) tantalum oxide, the metals of the oxides of (*a*) and (*b*) being present in such molar ratios that the total molar concentration of said metals ranges from 1.00 to 1.25 of the molar concentration of tantalum in said tantalum oxide.

6. A ceramic dielectric composition having a dielectric constant varying only slightly up to about 500° C., said composition being composed essentially of a vitrified combination of ingredients composed essentially of (*a*) an alkaline earth selected from the group consisting of strontium oxide, barium oxide, calcium oxide, and mixtures thereof, (*b*) a metallic oxide selected from the class consisting of zirconium oxide, titanium oxide, tin oxide, and mixtures thereof, and (*c*) tantalum oxide, the metals of

the oxides of (*a*) and (*b*) being present in such molar ratios that the total molar concentration of said metals is essentially equal to the molar concentration of tantalum in said tantalum oxide.

7. A ceramic composition having a dielectric constant varying only slightly up to about 350° C., said composition being a vitrified product of a mixture of ingredients composed essentially of (*a*) an alkaline earth selected from the class consisting of strontium oxide, barium oxide, calcium oxide, and mixtures thereof, (*b*) a metallic oxide selected from the class consisting of zirconium oxide, titanium oxide, tin oxide, and mixtures thereof, and (*c*) tantalum oxide, the metals of said oxides of (*a*) and (*b*) being present in such molar ratios in the vitrified product that there are from 1.25 to 1.75 mols of alkaline earth metal per 0.25 to 0.75 mol of the metal of said metallic oxide of (*b*), there being 0.75 to 1.50 mols of the combined metals in (*a*) and (*b*) to each one mol of tantalum in said tantalum oxide.

8. A ceramic composition having a dielectric constant varying only slightly up to about 350° C., said composition being a vitrified product of a mixture of ingredients composed essentially of (*a*) an alkaline earth selected from the class consisting of strontium oxide, barium oxide, calcium oxide, and mixtures thereof, (*b*) a metallic oxide selected from the class consisting of zirconium oxide, titanium oxide, tin oxide, and mixtures thereof, and (*c*) tantalum oxide, the metals of said oxides of (*a*) and (*b*) being present in such molar ratios in the vitrified product that there are from 1.25 to 1.75 mols of alkaline earth metal per 0.25 to 0.75 mol of the metal of said metallic oxide of (*b*), there being 1.00 to 1.25 mols of the combined metals in (*a*) and (*b*) to each one mol of tantalum in said tantalum oxide.

9. A ceramic composition having a dielectric constant varying only slightly up to about 500° C., said composition being a vitrified product of a mixture of ingredients composed essentially of (*a*) an alkaline earth selected from the class consisting of strontium oxide, barium oxide, calcium oxide, and mixtures thereof, (*b*) a metallic oxide selected from the class consisting of zirconium oxide, titanium oxide, tin oxide, and mixtures thereof, and

(*c*) tantalum oxide, the metals of said oxides of (*a*) and (*b*) being present in such molar ratios in the vitrified product that there are from 1.25 to 1.75 mols of alkaline earth metal per 0.25 to 0.75 mol of the metal of said metallic oxide of (*b*), the total molar concentration of the metals in (*a*) and (*b*) being equal essentially to the molar concentration of tantalum in said tantalum oxide.

10. A ceramic composition as defined in claim 6 wherein the molar ratio between the metal of said alkaline earth and the metal of said metallic oxides of (*b*) are present in such a ratio that there are 1.50 mols of said alkaline earth metal per 0.50 mol of the metal of said metallic oxide of (*b*).

11. A ceramic composition having a dielectric constant varying only slightly up to about 500° C., said composition being a vitrified product of a mixture of ingredients composed essentially of (*a*) an alkaline earth oxide selected from the class consisting of strontium oxide, barium oxide, calcium oxide, and mixtures thereof, (*b*) a metallic oxide selected from the class consisting of zirconium oxide, titanium oxide, tin oxide, and mixtures thereof, and (*c*) tantalum oxide, the metals of said oxides of (*a*) and (*b*) being present in such molar ratio in the vitrified product that there are from 1.25 to 1.75 mols of the alkaline earth metal for 0.25 to 0.75 mol of the metal of the metallic oxides of (*b*), the total molar concentration of the metals in (*a*) and (*b*) being equal to about 2 and being equal essentially to the same molar concentration of tantalum in said tantalum oxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,563,307	Burnham et al.	Aug. 7, 1951
2,646,359	Wainer	July 21, 1953
2,855,317	McQuarrie et al.	Oct. 7, 1958

FOREIGN PATENTS

755,860	Great Britain	Aug. 29, 1956

OTHER REFERENCES

Johnson et al.: J. American Ceramic Society, vol. 32, No. 12, December 1949 (pages 398–401).

UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 3,002,841 October 3, 1961

Gilbert Goodman

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

In the grant, lines 1, 2, and 3, for "Gilbert Goodman, of Schnectady, New York," read -- Gilbert Goodman, of Schenectady, New York, assignor to General Electric Company, a corporation of New York, --; line 12, for "Gilbert Goodman, his heirs" read -- General Electric Company, its successors --; in the heading to the printed specification, lines 3 and 4, for "Gilbert Goodman, 1099 Mohawk Road, Schenectady, N. Y." read -- Gilbert Goodman, Schenectady, N. Y., assignor to General Electric Company, a corporation of New York --.

Signed and sealed this 3rd day of April 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents