Dec. 18, 1962 G. GOODMAN 3,069,275

DIELECTRIC COMPOSITIONS

Filed Sept. 15, 1958 2 Sheets-Sheet 1

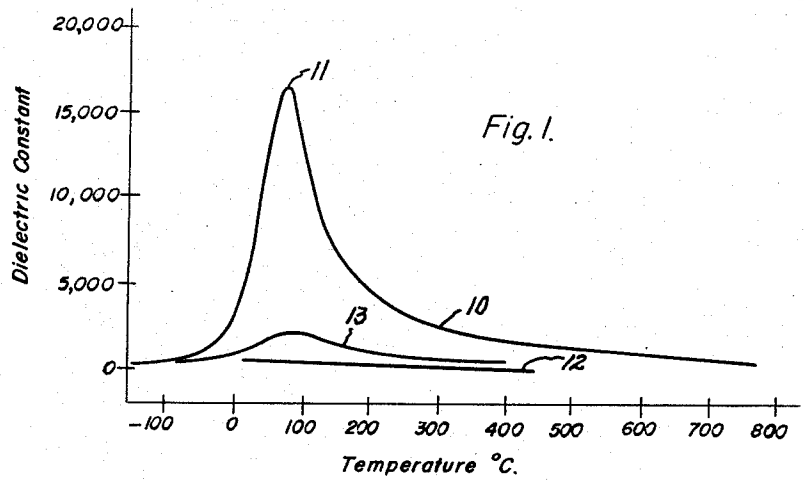


Fig. 1.

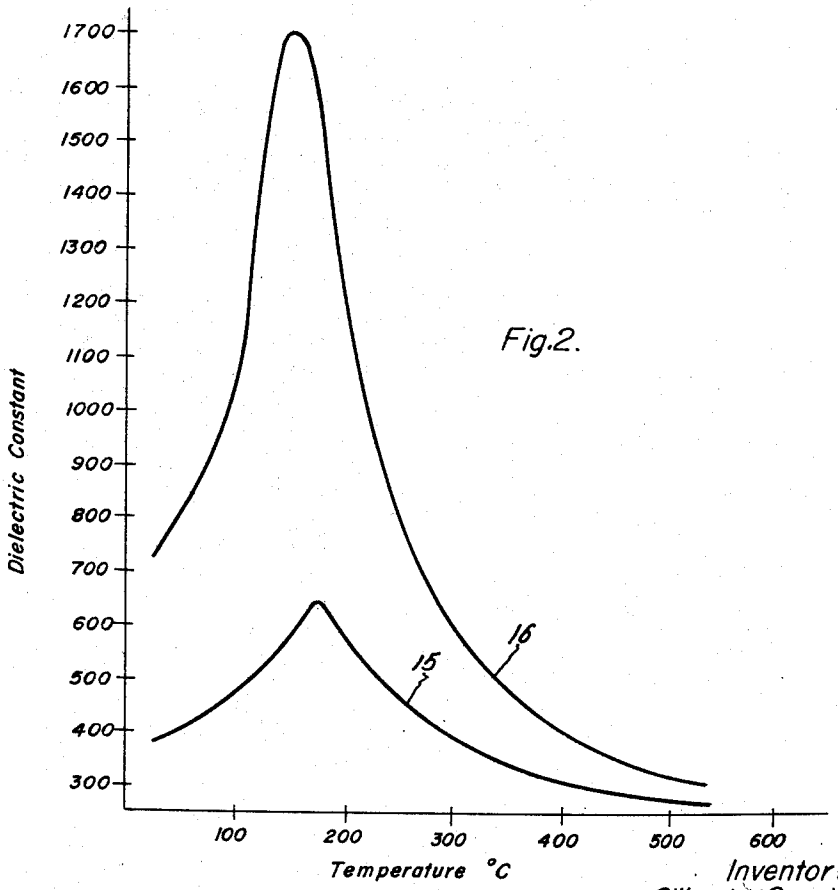


Fig. 2.

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DIELECTRIC COMPOSITIONS

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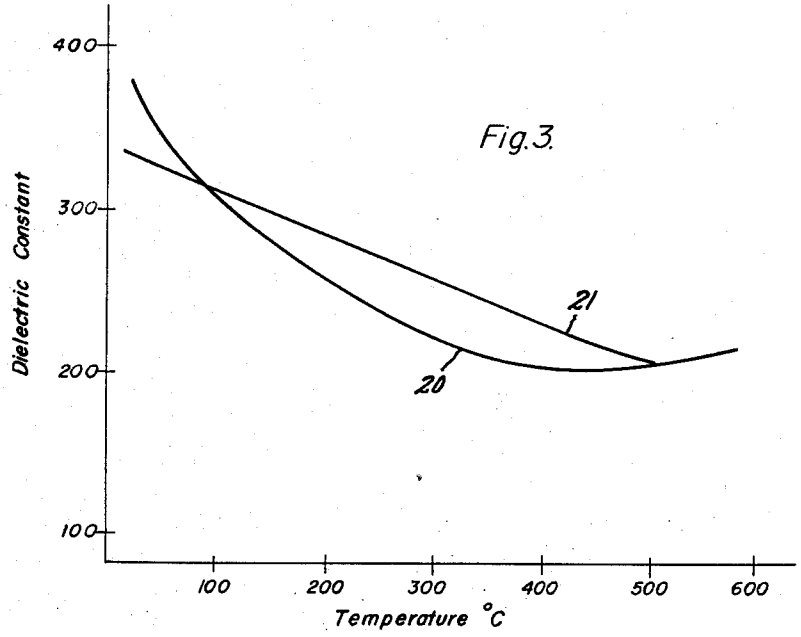


Fig. 3.

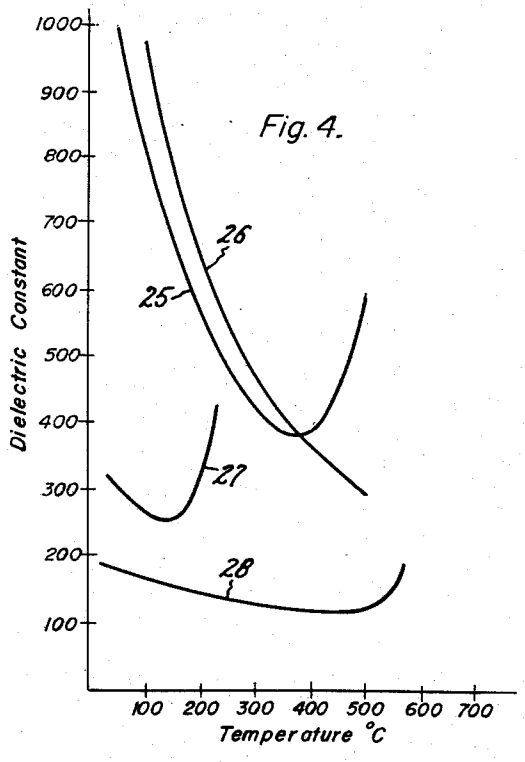


Fig. 4.

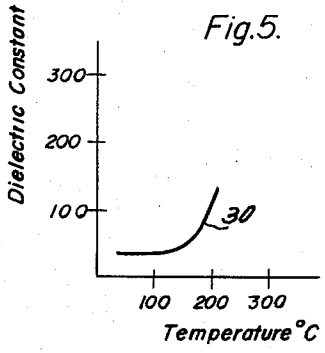


Fig. 5.

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DIELECTRIC COMPOSITIONS

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10 Claims. (Cl. 106—39)

This invention relates to dielectric compositions and more particularly to dielectric compositions displaying ferroelectric characteristics along a single crystal axis, which characteristics are retained at elevated temperatures.

The known ferroelectric substances can be divided generally into two groups: (1) substances like Rochelle salt, KH_2PO_4, and guanadine aluminum sulphate hexahydrate and their isomorphs; and (2) inorganic oxide compounds. Members of the first group are characterized by certain basic difficulties of use having to do with Curie temperatures located close to room temperature and with their solubility in water.

The prototype and most exploited member of the second group is barium titanate, $BaTiO_3$. Although it is most commonly used in the form of ceramics, certain applications such as computer memory circuits require single crystals. Moreover, other functions presently served by ceramics could be more advantageously performed by single crystals of suitable size and shape.

Since a barium titanate single crystal possesses a very slightly distorted cubic symmetry, it displays ferroelectric characteristics along any of its tetragonal axes; it also is subject to a Curie temperature at about 125° C. where the ferroelectric properties transform to paraelectric properties. The fact that ferroelectric properties can occur in more than one crystal direction gives rise to inherent difficulties when a crystal is used in certain situations.

For example, a barium titanate single crystal tends to lose its memory, or polarization, under conditions of aging or electrical or mechanical stress so that its use in computer circuits is limited. Such memory loss corresponds to partial changeover in one of the alternate ferroelectric directions. This would not occur in a crystal having a single ferroelectric direction. Also, when a single crystal or a polycrystalline ceramic body containing single crystals having the desired properties is to be used at elevated temperatures, as it would be in some electrical and electronic apparatus, it can no longer be depended upon to have the sought-after ferroelectric characteristics. This is, of course, due to a transition to the paralelectric state which occurs when the temperature exceeds the Curie temperature of the material.

It is therefore a principal object of this invention to provide a dielectric composition, single crystals of which display ferroelectric characteristics along a single crystal axis.

Another object of this invention is to provide a dielectric composition which has unidirectional ferroelectric characteristics and which has no observable Curie point up to the point of dielectric failure at an elevated temperature.

It is another object of this invention to provide a polycrystalline ceramic dielectric having a preferred ferroelectric direction and possessing no Curie point.

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

In the drawings:

FIG. 1 is a graph showing the effect of temperature on the dielectric constant of a single crystal and on a non-oriented ceramic body composed according to the present invention, the dielectric constant of the single crystal being measured along two crystal axes to show the unidirectional ferroelectric characteristics.

FIG. 2 is a graph of dielectric constants versus temperature as measured parallel to the ferroelectric direction, to show the absence of a Curie point;

FIG. 3 is a graph like that of FIG. 2 for additional dielectric compositions;

FIG. 4 is a graph showing the effect of compositional variations on the dielectric constant as a function of temperature; and

FIG. 5 is a graph showing the effect of temperature on the dielectric constant of a binary composition of barium and niobium oxides.

Generally, the present invention relates to dielectric compositions whose single crystals have (1) only one ferroelectric axis, (2) no Curie point, and (3) which can be formed into polycrystalline ceramic bodies having single crystal characteristics. These dielectrics are generally combinations of (*a*) a suitable alkaline earth fused together with (*b*) a metallic oxide from the group zirconium oxide, tin oxide and titanium oxide and (*c*) niobium oxide.

More specifically, the compositions of the present invention are preferably composed essentially of a vitrified or fused combination of (*a*) an alkaline earth selected from the group consisting of barium oxide and strontium oxide, and combinations thereof, (*b*) an oxide of one of the metals zirconium, titanium, or tin, or combinations thereof, which may be added as metal and subsequently oxidized and, as a final component, (*c*) niobium oxide.

It will be appreciated that the selected compositional components can be combined as metals and subsequently oxidized. 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. Early in the sintering or fusing process, the oxalate or carbonate will break down to form the oxide of the metal which then becomes part of the final product.

As already mentioned, while the compositions exhibit the strongest ferroelectric characteristics when in single crystal form, polycrystalline ceramic bodies can be formed, by suitable processing steps, which possess single crystal characteristics. That is, the polycrystalline bodies can be made to possess a single ferroelectric direction and to lack the normally existing Curie point.

The following Table I lists the nominal weight percent compositions of sample, polycrystalline bodies made according to the present invention.

Table I

No.	Ba-Oxalate [1]	$SrCO_3$ [2]	Nb_2O_5	TiO_2	SnO_2	ZrO_2	Firing Temp., ° C.
1	54.05		39.95	6.00			1,350
2		40.51	48.29			11.20	1,400
3		42.14	50.30	7.56			1,350
4	51.29		37.96		10.75		1,350
5		39.52	47.12		13.36		1,350
6	50.10		44.90			5.00	1,410

[1] Assay 64.0% BaO.
[2] Assay 69.72% SrO.

The ceramic bodies were made by mixing the quantities of the selected components listed in Table I in a ball mill in amyl acetate for between five and ten hours, the exact time of mixing not being critical as long as retained within the stated limits. Alcohol can be used in place of amyl acetate if desired. Following milling of the materials, they were dried and calcined in a platinum container at about 1200° C., crushed to −200 mesh, since it had agglomerated somewhat during firing, and carbowax was added to achieve consistency suitable for pressing the material into 1-inch diameter buttons, ⅛

inch thick. The buttons were then fired in air for 1 to 1½ hours on a platinum base at the temperatures indicated in Table I. Neither the temperature nor the time is particularly 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.

Ceramic bodies prepared as described above are polycrystalline structures containing primarily the ferroelectric crystal phase responsible for the unique properties claimed, and some additional material which may be considered dross. By removing the single crystals from the ceramic, bodies are obtained which have maximum dielectric constant values, no Curie point, and a single ferroelectric axis. The ceramics, as is to be expected, possess analogous physical and electrical properties except that the ferroelectricity is not unidirectional in character.

When single crystals are the primary objective, larger and more suitable samples are obtained by melting and recrystallizing the batch constituents than from sintering as described above. For example, if the mixed constituents of composition No. 6 in Table I are melted in a platinum crucible at 1540° C., cooled at a rate of 12° C. per hour to 1500°, and then more rapidly to room temperature, a solidified mass of crystals is obtained from which individuals can be easily extracted.

Referring to FIG. 1, the curves indicate the effect of temperature on the dielectric constant of a single crystal having the composition $4BaO3Nb_2O_5ZrO_2$. This crystal was obtained by preparing the ingredients of Sample 6 of Table I in the manner already described. It will be noted that although the initial composition was approximately $3BaO2Nb_2O_5ZrO_2$, the actual crystal composition was about $4BaO3Nb_2O_5ZrO_2$. This difference in composition between the starting materials and the final composition of a single crystal holds true for all of the compositions of this invention, owing to the incongruently melting nature of the material. Obviously, the overall composition of a ceramic body, as opposed to a single crystal, coincides with the starting composition.

Curve **10** illustrates the rounded maximum **11** through which the dielectric constant passes as the temperature is increased. The dielectric constant was measured parallel to the crystallographic C axis to obtained curve **10**, while the curve **12** illustrates the nature of the dielectric constant as measured along either the *a* or *b* crystallographic axis. In prior ferroelectric materials, the peak **11** of the curve **10** would normally represent the Curie point, at which temperature any existing ferroelectric properties convert to paraelectric properties. This is not the case with the present compositions since they continue to exhibit ferroelectric properties, such as hysteresis beyond the point of maximum dielectric constant. No evidence of a hysteresis loop is observed, on the other hand, at any point on curve **12**. When the initial composition $3BaO2Nb_2O_5ZrO_2$ is prepared and formed into an integral body, it possesses characteristics like those of the single crystals, but which are essentially an average of the dielectric properties along the three crystal axes. This is shown by curve **13** of FIG. 1 which falls between the curves **10** and **12**, these curves showing the extreme values along the crystal axes.

Whereas single crystal bodies have the highest dielectric constants and ordinary polycrystalline bodies the lowest ones, it is also possible to obtain polycrystalline ceramic masses which are composed largely of single crystals arranged in a common orientation. Thus, for example, if barium, niobium, and zirconium oxides are mixed in the mol ratios of 3 to 2 to 1, respectively, and lowered slowly in an elongated platinum crucible through a vertical tube furnace whose hot zone is above the melting point of the mixture, a boule, or ceramic body, having an oriented microstructure is obtained. In much of this boule, the structure consists of about 90% by volume of single crystals of $4BaO.3Nb_2O_5.ZrO_2$ whose crystallographic C-axes (the ferroelectric direction) are parallel and aligned along the long direction of the boule. As a result of this orientation, the boule possesses dielectric properties markedly better than those of conventional ceramics. For example, room temperature dielectric constants at 100 kc. per second for single crystals, conventional ceramics, and ceramics prepared as just described compare as follows.

Single Crystal (C-Axis)	Oriented Ceramics (growth direction)	Conventional Ceramic
6,500	1,160	250

The dielectric constants of other polycrystalline ceramic materials can be seen by reference to FIGS. 2 and 3 of the drawings, in which curves **15** and **16** of FIG. 2 show the dielectric constants of materials having the over-all compositions $3BaO2Nb_2O_5TiO_2$ and

$$3SrO2Nb_2O_5TiO_2$$

respectively. The dielectric constants peak through a rounded maximum and the materials possess ferroelectric properties beyond the maximum dielectric constant.

Curves **20** and **21** of FIG. 3 represent the temperature dependence of dielectric constant for the materials $3BaO2Nb_2O_5SnO_2$ and $3SrO2Nb_2O_5ZrO_2$ respectively. The maximum points do not appear in the temperature range presented, probably due to the fact that they occur somewhere below room temperature. However, both of these materials continue to exhibit ferroelectric properties up to relatively high temperatures.

Since we are concerned principally with the molar ratios between the metals, the following discussion deals essentially with the metals and refers to the oxides only when desirable for the sake of clarity.

An important factor to be considered, in order that the ternary composition have optimum dielectric and ferroelectric properties, is the molar ratio of the alkaline earth metal chosen to the metal selected from the (*b*) group of materials made up of zirconium, titanium, tin and combinations thereof. Generally, the alkaline earths and the zirconium, titanium, and tin oxides should be present in such molar ratios in the sintered 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 the chosen (*b*) group metal. That is, a ratio of 3 mols of alkaline earth metal, or combination of metals, to one 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 from group (*a*) to 0.5 mol of metal from the group (*b*) results in formation of a good dielectric which exhibits no Curie point and retains the ferroelectric properties up to relatively high temperatures.

While the foregoing molar ratios are preferred, other amounts can be used and still obtain a ceramic or a single crystal body having desirable properties which are unobtainable in most existing polycrystalline dielectrics. Thus, if instead of 1.5 mols of strontium to 0.5 of zirconium, for example, there is 1 mol of strontium to 1 mol of zirconium, improved properties are still obtained.

Similarly, the amount of niobium oxide used should create a definite molar relationship between the amount of niobium metal present and the total amount of the other two metals used from the (*a*) and (*b*) groups. Specifically, the total molar concentration of the (*a*) and (*b*) group metals preferably should substantially equal the amount of niobium metal present in its oxide. That is, if there are two mols of niobium present (Nb_2O_5), then the sum of the other two metals should

be 2 mols, so that substantially a 1-to-1 molar ratio is established.

The value of having a 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. 4 of the drawings. In the graph shown in this figure, the dielectric constants of the materials made of varying molar ratios between the metals of the (*a*) and (*b*) groups have been plotted against the temperature. Curves **25** and **26** show the dielectric constants of ternary compositions made up of $Ba_{1.5}Zr_{0.5}Nb_2O_5$. The difference in dielectric constants results from the fact that curve **25** resulted from measurements at 10 kilocycles, whereas curve **26** resulted from measurements taken at 1 megacycle. The effect of increasing the frequency at which the dielectric constant of the material is measured is to depress the maximum and to shift it toward a higher temperature. Since the peak for this material is quite high and occurs below room temperature, the maximum points do not show but the lateral shift to a higher temperature can quite readily be seen. Also, the apparent increase in dielectric constant indicated by the upwardly extending right hand end of curve **25** as viewed in the drawing as well as curves **27** and **28** is actually a conduction effect.

Referring to curve **27** of FIG. 4, the ternary composition contained 1.75 mols of barium to 0.25 mol of zirconium and 2 mols of niobium. Thus, the combined molar amounts of barium and zirconium are equal to the total amount of niobium present so that a 1-to-1 ratio is present. On the other hand, curve **28** shows the dielectric constant of a material containing 1.0 mol of barium, 0.5 mol of zirconium and 2 mols of niobium. Thus, in the latter material there are 1.5 mols of barium and zirconium to 2 mols of niobium and the 1-to-1 ratio is no longer present. It is quite apparent that the dielectric constant for the 1-to-1 ratio will peak higher, and at a higher temperature, than will the 1.5 to 2 ratio. Also, the flattening out of curve 28 indicates that the ferroelectric properties are marginal and that paraelectric properties will replace them if the ratio is lowered still further from the desired 1 to 1.

Comparison of the curves **25** through **28** clearly indicates that the best molar relationship exists when 1.5 mols of barium or other alkaline earth metal to 0.5 mol of zirconium, tin, titanium or some combination thereof are present. Such material peaks at a higher dielectric constant value and at a higher temperature than it does when the ratio is changed either by varying the amount of the alkaline earth metal with respect to the zirconium, tin, etc. from (*b*) group or by changing the molar ratio between the total amounts of the (*a*) and (*b*) group components with respect to the niobium.

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 barium, and 2 mols of niobium, so that it is a binary composition. The low and relatively temperature-independent dielectric constant indicates a complete absence of ferroelectric properties. The upturned end of curve 30 is a conduction effect.

Thus, this invention provides dielectric compositions which can be used for high temperature applications where ferroelectric properties are desired and are further valuable where a single direction of polarization is either required or desired.

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

1. A single crystal dielectrtc body consisting essentially of a fused combination of (*a*) 4 mol parts of an alkaline earth selected from the group consisting of barium oxide, strontium oxide and combinations thereof, (*b*) one mol part of a metallic oxide selected from the group consisting of zirconium oxide, titanium oxide, tin oxide and combinations thereof, and (*c*) 3 mol parts of niobium oxide, said single crystal body exhibiting ferroelectric properties along a single crystal axis.

2. A dielectric composition as defined in claim 1 wherein said alkaline earth is barium oxide.

3. A dielectric body consisting essentially of a fused combination of (*a*) an alkaline earth selected from the group consisting of barium oxide, strontium oxide and combinations thereof, (*b*) a metallic oxide selected from the group consisting of zirconium oxide, titanium oxide, tin oxide and combinations thereof, the metals of said oxides of (*a*) and (*b*) being present in such molar ratios 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*), and (*c*) niobium 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 about .75 to about 1.25 of the molar concentration of niobium in said niobium oxide.

4. A dielectric composition as defined in claim 9 wherein said (*a*) group alkaline earth is strontium oxide and said (*b*) group metal oxide is titanium oxide.

5. A dielectric body as defined in claim 6 wherein the total molar concentration of the metals in (*a*) and (*b*) is equal essentially to the molar concentration of niobium in said niobium oxide.

6. A dielectric body as defined in claim 3, wherein the molar ratio between the metal of said alkaline earth and the metal of said metallic oxides is 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*).

7. A dielectric body consisting essentially of a fused combination of (*a*) an alkaline earth selected from the group consisting of barium oxide, strontium oxide and combinations thereof, (*b*) a metallic oxide selected from the group consisting of zirconium oxide, titanium oxide, tin oxide and combinations thereof, and (*c*) niobium oxide, the metals of said oxides of (*a*) and (*b*) being present in such molar ratio that there are from 1.25 to 1.75 mols of the alkaline earth metal per 0.25 to 0.75 mol 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 molar concentration of niobium in said niobium oxide.

8. A polycrystalline body containing oriented crystals causing said body to have essentially unidirectional ferroelectric properties, said body consisting essentially of a fused combination of (*a*) an alkaline earth selected from the group consisting of barium oxide, strontium oxide and combinations thereof, (*b*) a metallic oxide selected from the group consisting of zirconium oxide, titanium oxide, tin oxide and combinations thereof, the metals of said oxides of (*a*) and (*b*) being present in such molar ratios 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*), and (*c*) niobium oxide, the metals of the oxides of (*a*) and (*b*) being present in such molar ratios that the total concentration of said metals ranges from about .75 to about 1.25 of the molar concentration of niobium in said niobium oxide.

9. A single crystal dielectric body consisting of a combination of (*a*) barium oxide, (*b*) zirconium oxide and (*c*) niobium oxide, the three metallic oxides being combined in proportions such that the composition of said body is represented by the formula $4BaO3Nb_2O_5ZrO_2$.

10. A dielectric ceramic composition consisting essentially of a mixture of (*a*) barium oxide, (*b*) a metal oxide selected from the group consisting of zirconium oxide and titanium oxide and (*c*) niobium pentoxide, with molar ratios of (*a*):(*b*) being between about 5:1 and 2.5:1 and the molar ratio of (*a*)+(*b*):(*c*) being between about .75 and 1.17.

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