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DIELECTRIC COMPOSITIONS

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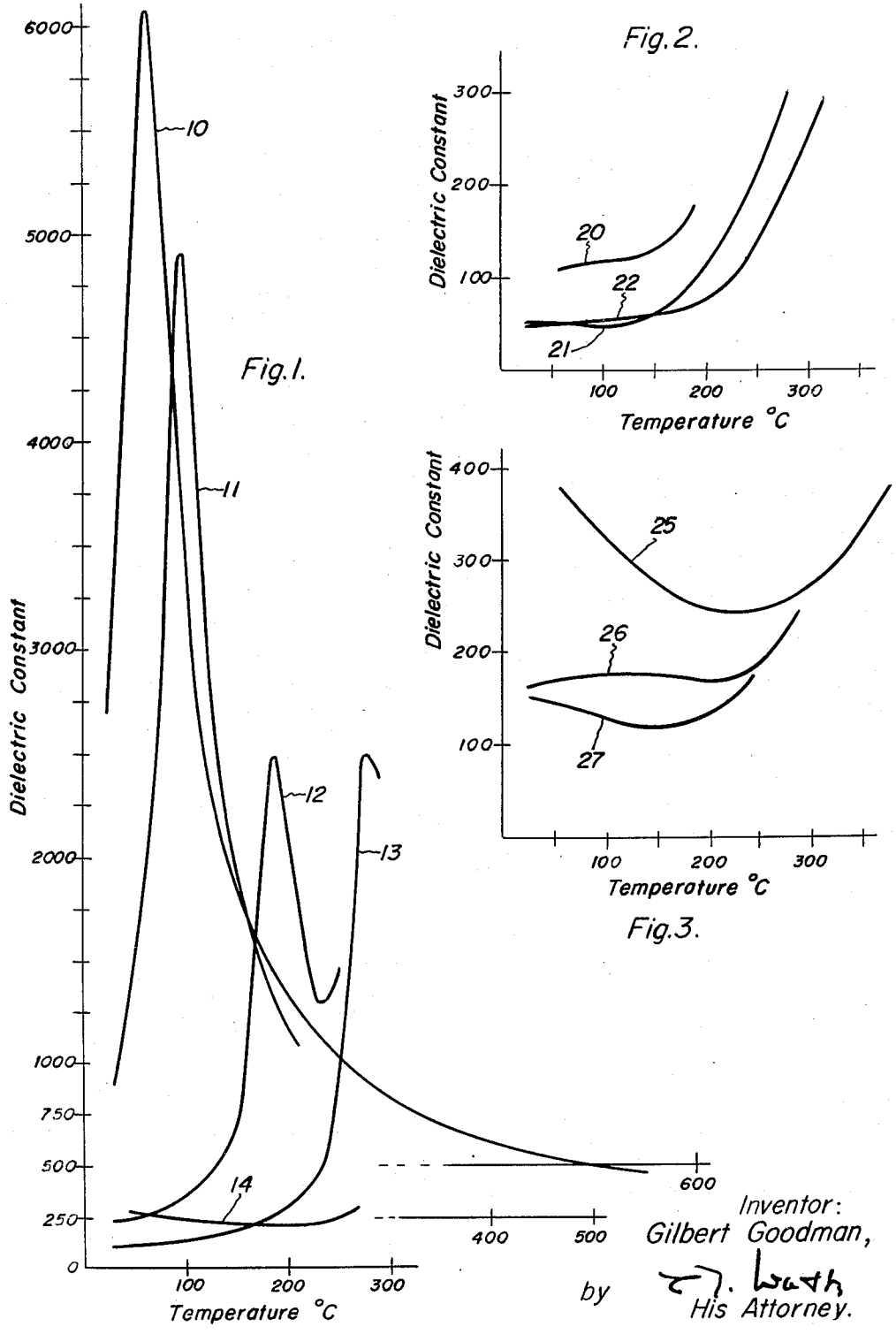


Fig. 1.

Fig. 2.

Fig. 3.

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DIELECTRIC COMPOSITIONS

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This invention relates to dielectric compositions and more particularly to dielectric compositions displaying ferroelectric characteristics which within their useful temperature range are not subject to a Curie temperature at which transition to paraelectric behavior occurs, and further relates to bodies made of such dielectric compositions.

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. The members of the first group are subject to severe limitations in use due to certain basic difficulties having to do with Curie temperatures located close to room temperature, and with their solubility in water.

Barium titanate, $BaTiO_3$, is the prototype and most exploited member of the second group, and it is most commonly used in the form of ceramics, although in applications such as computer memory circuits, single crystals are utilized. Barium titanate is subject to a Curie temperature of about 125° C., where the ferroelectric properties transform to paraelectric properties. Obviously, when either a barium titanate ceramic body or a barium titanate single crystal must be used at elevated temperatures, as they would be in some electrical and electronic apparatus, they can no longer be depended upon to have the desired ferroelectric characteristics.

It is therefore a principal object of this invention to provide a dielectric composition which has no observable Curie point up to the point where conduction becomes dominant at an elevated temperature and the material is no longer useful as a dielectric.

It is another object of this invention to provide ceramic or single crystal dielectric bodies which can be used at elevated temperatures and still possess ferroelectric properties.

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 constants of various compositions made according to the present invention;

Fig. 2 is a graph showing the effect of temperature and compositional variations on the dielectric constants of additional compositions;

Fig. 3 is a graph which also shows the relationship of compositional and temperature variations on the dielectric constants of the compositions.

Generally, the present invention relates to dielectric compositions and to bodies made of dielectric compositions which exhibit no Curie point up to the temperature where condition becomes dominant. These dielectrics are generally combinations of (*a*) barium oxide (*b*) strontium oxide and (*c*) niobium oxide, fused together into a ceramic body.

More specifically, the compositions of the present invention are preferably composed essentially of a vitrified

or fused combination of (*a*) barium oxide, (*b*) strontium oxide, and (*c*) niobium oxide, the combined molar amounts of strontium and niobium metals in oxide form being present in predetermined amounts with respect to the molar quantity of niobium metal present as niobium oxide.

When preparing a mixture of the selected components, it will be appreciated they can be combined as metals and subsequently oxidized, or, as is done in most instances, the materials can be combined as oxides since they are normally more readily and inexpensively obtainable in this condition. They may also be added as oxygen-containing compounds, such as barium and strontium oxalates and/or carbonates noted in the following Table I, as early in the sintering or fusing process the oxalates or carbonates will break down to form the oxide of the metal, which then becomes part of the final product.

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

Table I

Sample No.	Composition—Weight Percent			Firing Temp. and Time
	Ba-Oxalate*	$SrCO_3$**	Nb_2O_5	
10	20.03	20.71	59.25	1,350° C., 3 hrs.
11	26.05	16.17	57.76	1,350° C., 3 hrs.
12	31.78	11.82	56.37	1,400° C., 3 hrs.
13	37.23	7.70	55.07	1,425° C., 3 hrs.
14	13.71	25.50	60.77	1,400° C., 3 hrs.
20	36.63	22.74	40.61	1,350° C., 1 hr.
21	51.39	10.62	37.99	1,350° C., 1 hr.
22	19.68	36.63	43.68	1,350° C., 1 hr.
27	45.60	9.45	44.95	1,350° C., 3 hrs.
26	32.28	20.02	47.70	1,350° C., 1 hr.
25	17.19	31.98	50.81	1,350° C., 1 hr.

* Assaying 64.0% BaO.
**Assaying 69.72% SrO.

Ceramic bodies having the preceding compositions were made by mixing the quantities of the selected components listed in Table I in a ball mill in amyl acetate for between 5 and 10 hours, the exact time for 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. for 3 hours, crushed to —200 mesh, because of the agglomeration which accompanied calcination, and Carbowax was added to achieve consistency suitable for pressing the material into one inch diameter buttons, ⅛ inch thick. The buttons were then fired in air on a platinum base at the temperatures and for the times indicated in Table I. Neither the temperature nor the time is particularly critical, as the time at maximum temperature may vary as much as one hour and the maximum temperature as much as 25° C., for example.

Ceramic bodies prepared as outlined above are polycrystalline structures containing primarily a ferroelectric crystal phase responsible for the unique properties, and some additional material which may be considered dross. By removing the single crystals from the ceramic, bodies are obtained which have maximum dielectric values. On the other hand, for many applications the properties possessed by polycrystalline bodies are suitable, since they are qualitatively similar to the properties of a single crystal.

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 previously. For example, if mixed constituents of composition #10 of Table I are heated in a

platinum crucible to 1600° C., cooled at a rate of 10° C. per hour to 1400° C., and then cooled more rapidly to room temperature, a solidified mass of crystals is obtained from which such individual crystals can be easily extracted.

Referring to the drawings to illustrate the properties of dielectric bodies made according to the present invention, the curves are numbered to correspond with the compositions shown in Table I. In Fig. 1 the curves indicate the effect of temperature on the dielectric constant of ceramics in which the total amount of barium and strontium present in the oxides is equal essentially to half the amount of niobium metal present as niobium oxide. While the total combined amount of barium and strontium is about one-half that of the niobium, the amounts of barium and strontium are varied so that the ratio between the two metals is different for each of the samples used to obtain the four curves. This procedure was adopted to determine the effect of compositional variations on the dielectric constants at different temperatures.

The curves of Fig. 1, specifically **10–13**, indicate that the dielectric constant passes through a rounded maximum and then decreases at about the same rate as the increase initially occurred. In prior ferroelectric materials, dielectric constant maxima or peaks corresponding to those of the curves in Fig. 1, normally represent the Curie point, where 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 region of maximum dielectric constant. The maxima in the curves are associated with a dielectric relaxation.

Referring specifically to curve **10**, the barium metal, which as already mentioned, is present as the oxide in the completed ceramic, is present in an amount such that there is a ratio of 0.375 mol of barium to 0.625 mol of strontium metal, the latter also being present in oxide form. Thus, the combined amount of barium and strontium is equal to 1 mol and the niobium metal is present in an amount of 2 mols. In curve **11** the ratio has been changed so that the amount of barium has been increased to 0.5 and the strontium decreased to 0.5. Similarly, in curves **12** and **13** the barium is increased to 0.625 and 0.75 mol respectively and the strontium decreased to 0.375 and 0.25 mol, respectively. Two mols of niobium are present in all compositions.

The composition whose properties are represented by curve **14** of Fig. 1 contains 0.25 mol of barium, 0.75 mol of strontium and 2 mols of niobium. In this instance, the maximum has apparently been shifted to such a low temperature that the maximum is not shown.

Comparing all of the curves, it will be seen that the relative increase in the amount of barium and decrease in the amount of strontium results in a lowering of the maximum dielectric constant and a shifting of the maximum point to higher temperatures. This effect can, of course, be utilized where it is desired to have a dielectric material which has a relatively high dielectric constant at elevated temperatures. The dielectric constant measurements for curve **10** where taken at a frequency of 1 megacycle per second whereas the dielectric constant measurements for curves **11–14** were made at 1 kilocycle per second.

Although single crystal bodies have the highest dielectric constants and ordinary polycrystalline bodies have the lowest ones, it is possible to obtain polycrystalline masses which are composed largely of single crystals arranged in a common orientation. Thus, for example, if barium, strontium, and niobium oxides are mixed in the mol ratios of 0.5 to 0.5 to 1, respectively, and lowered slowly in an elongated platinum crucible through a 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 crystals having common axes aligned in parallel relationship. As a result of this orientation the boule possesses dielectric properties intermediate between those of a single crystal and those of a conventional ceramic.

An important factor to be considered, in order that the ternary composition have optimum dielectric and ferro-electric properties, is the molar ratio existing between the combined amounts of barium and strontium metals present and the amount of niobium metal present. Specifically, the total molar concentration of the (*a*) and (*b*) group metals (barium and strontium) preferably should equal approximately one-half the amount of niobium metal present in its oxide. That is, if there are 2 mols of niobium present, then the sum of the barium and strontium metals should be 1 mol so that substantially 0.5 to 1 molar ratio is established.

Generally, in order for optimum properties to be achieved, the dielectric body should contain, for each 2 mols of niobium present as niobium oxide, from 0.25 to 0.75 mol parts or barium as barium oxide and from 0.25 to 0.75 mol parts of strontium as strontium oxide. The total combined amounts of barium plus strontium present may vary from 0.75 mol to not more than about 1.50 mols, amounts on either side of this range reducing the results to the point where they are unacceptable for normal dielectric purposes.

Referring to Fig. 2 of the drawings, curves **20**, **21** and **22** illustrate the effects of varying the ratio between the total amount of barium and strontium and the total amount of niobium, as well as the effect of changing the ratio between the barium and strontium. In all cases, however, there are two mols of barium and strontium for each two mols of niobium, this resulting in a 1 to 1 mol ratio. The curve **20** shows the effect of temperature on the dielectric constant of a ceramic body made according to the previously described process and containing metals in the mol ratios of 1.0Ba:1.0Sr:2.0Nb. It will be noted that the dielectric constant apparently increases slightly up to about 125° C., at which time it appears to increase rapidly toward a maximum value. Actually, the upward trend of the curve **20** results from a conduction effect indicating deterioration of dielectric properties. Ultimately the deterioration proceeds to the point that the material is no longer useful as a dielectric.

Dielectric values essentially similar to those indicated by curve **20** are shown by curves **21** and **22**. Here, the dielectric constants are substantially invariant up to temperatures around 150° C., where after there begins the apparent rise from a conduction effect. These dielectrics have metal mol ratios of 1.5Ba:0.5Sr:2.0Nb, and 0.5Ba:1.5Sr:2.0Nb, respectively.

Curves **25** through **27** of Fig. 3 were obtained by using ceramic bodies in which the combined amount of barium and strontium provided 1.5 mols of these materials for each 2 mols of niobium. In these ceramics the mol proportions of barium and strontium are: 0.375Ba:1.125Sr: 0.75Ba:0.175Sr; and 1.125Ba:0.375Sr for curves **25**, **26** and **27** respectively. These ceramics have dielectric constants which peak at fairly low temperatures, although ferroelectric properties are retained up to elevated temperatures where the conduction effect begins to take place.

Thus, this invention provides dielectric compositions which can be used for high temperature applications where ferroelectric properties are desired and where relatively high dielectric constants are either needed or preferred.

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

1. A dielectric body consisting essentially of a combination of (*a*) barium oxide, (*b*) strontium oxide, and niobium oxide, the barium and strontium metals of the oxides of groups (*a*) and (*b*) being present in such molar ratio that there are from 0.25 to 0.75 mol of barium pres-

ent per 0.75 to 0.25 mol of strontium, the total molar concentration of barium and strontium being equal to about 1 and being equal essentially to ½ the molar concentration of niobium in said niobium oxide.

2. A dielectric body consisting essentially of a combination of (*a*) barium oxide, (*b*) strontium oxide, and (*c*) niobium oxide, barium and strontium metals of the oxides of group (*a*) and (*b*) being present in such molar ratios that they are from 0.375 to 0.625 mol of barium present per 0.625 to 0.375 mol of strontium, the total molar concentration of barium and strontium being equal to about 1 and being equal essentially to ½ the molar concentration of niobium in said niobium oxide.

3. A dielectric body as defined in claim 2 wherein said barium and said strontium are present in 0.5 mol quantities.

4. A dielectric body consisting essentially of (*a*) 0.25 to 0.75 mol parts of barium as barium oxide, (*b*) 0.25 to 0.75 mol parts of strontium as strontium oxide, and (*c*) 2 mol parts of niobium as niobium oxide, the total amount of barium and strontium present ranging from not less than about 0.75 to not more than about 1.50 mols.

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