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HIGH DIELECTRIC MATERIAL

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This invention relates to ceramic dielectric materials. More particularly, it relates to such materials in which compounds of titanium are the predominating constituent used in combination with compounds of zirconium and tin.

In previous applications for patent, namely, Serial No. 482,613 filed April 10, 1943, now Patent No. 2,420,692 of May 20, 1947; Serial No. 489,382 filed June 2, 1943, now Patent No. 2,377,910 of June 12, 1945; Serial No. 490,485 filed June 11, 1943, now Patent No. 2,402,515 of June 18, 1946, and Serial No. 377,851 filed February 7, 1941, now Patent No. 2,371,660 of March 20, 1945, the useful properties of mixtures of alkaline earth titanates, of certain titanates and fluorides, of titanates and stannates and of titanium with certain metal oxides have been described and claimed. The present invention relates to another group of bodies prepared by compounding titanates ceramically with zirconates and stannates whose usefulness is equally widespread. This novel group of ceramic compositions have properties such as to make them useful as capacitors in radio, television, and communications generally, as capacitative temperature compensating devices in receivers and communication equipment to prevent distortions due to changes in circuit characteristics caused by temperature changes. The dielectric constants of some of these compositions are so high as to make possible their utilization in low frequency distribution and communication systems such as 60 cycle lines, by means of capacitative coupling between a low frequency high tension transmission line and communication telephone lines. Further, these high constants enable those materials to be used as substitutes for high capacity paper and electrolytic type condensers for by-pass, filter, and power circuits, for use in radio, fluorescent lighting circuits, etc.

Further, the very high dielectric constants make possible the use of these materials as electro-mechanical devices, for example, the transfer of mechanical energy or motion into electrical energy or vice versa, in a fashion similar to the action exhibited by piezoelectric crystals. Thus the novel compositions of the present invention have possible utility in pyroelectricity, supersonics, crystal or condenser microphones, frequency stabilizers, loud speakers, phonograph pick ups, telephone design, and oscillator designs generally. The foregoing remarks apply particularly to those bodies whose dielectric constants are over 1000 at radio frequency. In condenser microphones, very thin sheets of the higher dielectric constant materials are rigidly clamped at either center or edges and used as vibrating diaphragms. The minute changes of dimension or position of the dielectric due to vibration will occasion relatively large changes in capacity by means of which sound is transformed into electrical energy.

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Other members of this group, particularly those having dielectric constants over 1000 appear to exhibit electrical and mechanical characteristics of the same nature as piezoelectrical and pyroelectrical crystals. For example, a rod of the material having one end fixed and one end free to vibrate will develop a potential difference of several volts between the two ends of the rod, when in vibration.

The particular usefulness of this group as compensators for correction of frequency drift lies not only in the possibility of obtention of both positive and negative temperature coefficients of a wide variety but also the possibility of controlling the variation through choice of the proper composition. Furthermore, some of the temperature coefficients make members of the group useful as mica substitutes, particularly because of the low power factors available.

These novel compositions consist broadly of fired mixtures of the titanates of the alkaline earths, particularly barium titanates, with the zirconates and stannates of the alkaline earths. The alkaline earth compounds generally are of utility for this invention, including those of magnesium, calcium, strontium and barium. The peculiarly beneficial effect of the zirconate-stannate additions is most strikingly shown in the case of additions to $BaTiO_3$. At radio frequencies barium titanate has a dielectric constant of 1200–1300, and a temperature coefficient which is first negative, then strongly positive, and finally strongly negative between 20° and 150° C. Not only may this erratic behavior be eliminated by addition of the zirconates and stannates to barium titanate but dielectric constants of the order of several thousand are common.

In the practice of the present invention, the ingredients as indicated in the table below are properly reacted ceramically and then ground so that the coarsest particles will pass a 325 mesh screen. The dried powders are then mixed within the limits indicated by the proportions given in the table. Approximately 10% water is added and thoroughly mixed in the damp powder, granulated by passage through a 20 mesh screen. They are then pressed in a die under a pressure of 5 to 10 tons per square inch, and then allowed

to air dry for 24 hours. The pieces used for the purposes of this specification are roughly 1 inch in diameter and 0.1 inch thick. Pieces of such size are fired on a schedule of 400° F. per hour to the peak temperature, then held at peak temperature for three hours, and then allowed to cool. The maturation temperature for all the bodies listed below is between 2450° F. and 2500° F. After cooling, the opposing parallel surfaces are painted with silver powder paste which is fixed as a silver electrode by firing to 1500° F.

The values obtained below were determined at one megacycle, using a radio frequency bridge of standard design. Resistivity was determined on a high sensitivity resistance circuit on which a resistance of a million megohms could easily be detected, the zero point indicator being a galvanometer. The 1000 cycle measurements were obtained through use of an impedance bridge of standard design, whose arms were resistive components.

The data below indicate that not only may these groups of compositions be used for by-pass, filter, and power pack condensers as substitutes for paper and electrolytics but also as substitutes for mica both from standpoint of power factor and temperature coefficient. The possibility of variation and control of temperature coefficients is indicated from Table 2. These data were obtained at one megacycle.

TABLE 1

Comp. No.	Parts by weight of Titanate	Zirconate	One Megacycle		One Kilocycle	
			Dielectric Constant	Power Factor	Dielectric Constant	Power Factor
				Per cent		*Per cent*
37	90 $BaTiO_3$+10	$BaSnO_3$+1 $BaZrO_3$	3,950	2.85	4,550	1.7
38	90 $BaTiO_3$+10	$BaSnO_3$+2 $BaZrO_3$	5,050	3.73	5,850	1.9
39	90 $BaTiO_3$+10	$BaSnO_3$+3 $BaZrO_3$	4,300	3.70	4,920	1.7
40	90 $BaTiO_3$+10	$BaSnO_3$+5 $BaZrO_3$	4,050	3.36	5,200	1.8
41	90 $BaTiO_3$+10	$BaSnO_3$+7 $BaZrO_3$	3,190	1.61	3,575	4.3
42	90 $BaTiO_3$+10	$BaSnO_3$+10 $BaZrO_3$	3,310	1.04	3,740	4.3
43	100 $BaTiO_3$+1	$BaSnO_3$+3 $MgZrO_3$	3,010	1.57	----------	----------
44	100 $BaTiO_3$+3	$BaSnO_3$+3 $MgZrO_3$	3,000	1.40	----------	----------
45	100 $BaTiO_3$+5	$BaSnO_3$+3 $MgZrO_3$	2,770	1.73	----------	----------
46	100 $BaTiO_3$+7	$BaSnO_3$+3 $MgZrO_3$	2,860	1.62	----------	----------
47	100 $BaTiO_3$+10	$BaSnO_3$+3 $MgZrO_3$	3,010	1.34	----------	----------
48	100 $BaTiO_3$+15	$BaSnO_3$+3 $MgZrO_3$	3,050	0.96	----------	----------
49	100 $BaTiO_3$+20	$BaSnO_3$+3 $MgZrO_3$	2,500	0.76	----------	----------
50	100 $BaTiO_3$+25	$BaSnO_3$+3 $MgZrO_3$	2,250	0.71	----------	----------

TABLE 2

Temperature coefficient of capacity

Temp., °C.	Body #37	Body #38	Body #39	Body #40	Body #41	Body #42	Body #43	Body #44	Body #45	Body #46	Body #47	Body #48	Body #49
30	3,980	4,920	4,220	4,270	3,320	3,690	2,930	3,130	2,660	2,950	3,510	3,050	2,930
40	4,180	5,160	4,380	4,660	3,640	3,790	2,940	3,130	2,710	2,990	3,510	3,030	2,885
50	4,480	5,510	5,070	4,920	3,830	3,980	2,955	3,140	2,790	3,030	3,510	2,930	2,750
60	4,960	6,230	5,670	5,750	4,180	4,160	2,970	3,160	2,830	3,100	3,490	2,810	2,680
70	5,560	6,630	6,550	6,510	4,540	4,180	2,970	3,175	2,910	3,120	3,440	2,690	2,590
80	6,460	7,480	7,560	7,450	4,840	4,240	2,970	3,175	2,960	3,100	3,340	2,620	2,440
90	7,040	8,080	9,180	8,060	4,970	4,210	2,970	3,140	2,960	3,050	3,220	2,490	2,290
100	7,110	8,440	10,400	8,130	4,920	4,070	2,970	3,120	2,960	2,940	3,080	2,360	2,120
110	7,000	8,150	10,200	7,400	4,580	3,730	2,920	3,020	2,920	2,830	2,870	2,210	2,020
120	5,810	7,200	8,840	6,560	4,140	3,330	2,810	2,850	2,830	2,690	2,660	2,020	1,840
130	4,830	5,790	7,100	5,180	3,210	2,880	2,630	2,610	2,650	2,500	2,450	1,785	1,690
140	3,980	4,530	4,930	4,180	2,970	2,550	2,460	2,380	2,430	2,420	2,250	1,685	1,570
150	3,250	3,180	3,920	3,180	2,520	2,190	2,250	2,210	2,320	2,110	2,030	1,550	1,450

The temperature coefficients of the compositions listed are indicative of the scope of variation possible. While single compositions may yield the desired coefficient, an infinite variety of coefficient is possible through parallel combination of one or more bodies.

The special characteristics of the titanate, stannate, zirconate compositions are as follows, the relatively low stannate-magnesium zirconate addition to barium titanate produce dielectric materials which, as a group, exhibit an almost flat temperature variation of capacity over a range of nearly 60° C. They thus cover the complete range of household temperatures. The last three compositions are smoothly negative and exhibit the flattest temperature curves of a positive-neutral-negative type of any series investigated thus far. Furthermore, such temperature characteristics are available with the highest dielectric constant yet developed for this type of temperature variant dielectric.

From the foregoing, it will be seen that the stannates, titanates and zirconates of the alkaline earth metals including magnesium can be combined ceramically to provide useful dielectric materials wherein the dielectric contains two or more of these chemicals. All of these substances have the same crystal lattice structure as the calcium titanate mineral perovskite, namely, a face centered body centered cube. The invention is, therefore, directed to ceramic mixture of two or more substances having the perovskite structure.

What is claimed is:

1. A dielectric composition comprising an alkaline earth titanate, an alkaline earth stannate and and an alkaline earth zirconate.

2. A dielectric composition comprising an alkaline earth titanate, an alkaline earth stannate and magnesium zirconate.

3. A dielectric composition comprising an alkaline earth titanate, barium stannate and magnesium zirconate.

4. A dielectric composition comprising barium titanate, barium stannate and magnesium zirconate.

5. A dielectric composition comprising barium titanate in major amount and an alkaline earth

stannate and an alkaline earth zirconate in minor amount.

6. A dielectric composition comprising barium titanate in major amount and barium stannate and an alkaline earth zirconate in minor amount.

7. A dielectric composition comprising barium titanate in major amount and barium stannate and magnesium zirconate in minor amount.

8. A dielectric composition comprising the titanate, stannate and zirconate of barium.

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