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HIGH DIELECTRIC CONSTANT CERAMICS

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The present invention relates to dielectric materials and particularly to ceramic dielectrics that are extremely resistant to extremes of temperature and to rapid changes of temperature.

Specific high dielectric constant materials are described in pending applications for patent, Ser. No. 465,387, filed November 12, 1942, and Ser. No. 482,613, filed April 10, 1943. The materials there described consist essentially of alkaline earth titanates with, in some instances, additions of other materials. These high dielectric constant materials are ceramic bodies which, when properly matured and fired, develop high dielectric constants at radio frequencies from 275 to 10,000 kilocycles.

For many uses, the properties developed by such alkaline earth titanates are very useful, but for certain specialized requirements, defects are exhibited which limit their usefulness. These specialized applications usually involve the employment of the dielectric at extremes of temperature of -60° to $+150^{\circ}$ C. in which employment the change of temperature may be extremely rapid. Such rapid temperature changes and extremes are encountered in aircraft in flight and in automotive engines or components in close association with such engines. Under such extremely severe service conditions, the alkaline earth titanates such as barium titanate and barium-strontium titanate exhibit two important defects. First, these ceramics will not withstand the necessary thermal shock without shattering, and secondly, their dielectric constants fluctuate relatively wildly with wide variations in temperature.

A standard laboratory test for such materials, from a thermal shock standpoint, is the immersion of a standard size test specimen in boiling water for ten minutes, followed by rapid plunging into water in equilibrium with ice, in which bath it will remain for ten minutes. A satisfactory body should withstand at least 20 such cycles without shattering; the present invention provides compositions providing such bodies. Pure barium titanate usually fails completely in the first or second cycle. Although the temperature coefficient of barium titanate is satisfactory up to 75° C. or 80° C., at this point the dielectric constant starts to rise rapidly and if the temperature rise is made slow enough a pronounced peak of capacity, 3 to 5 times the room temperature level, is obtained at 120° C. to 130° C. This change in capacity with temperature appears to be the incidence of an allotropic change involving a wide volume change.

In accordance with the present invention it has been found that the addition of certain fluorides to barium titanate eliminates the difficulties and defects mentioned above. When the proper fluoride is used the fired bodies are completely resistant to the heat shock test listed above, the compositions withstanding hundreds of such cycles without fracturing. Secondly, and more important, temperature coefficients are obtained which make the compositions useful for the commercial applications mentioned above, in that peak development of capacity at elevated temperatures is eliminated.

The novel results are accomplished by adding the fluorides of magnesium or calcium to barium titanate, mixing thoroughly and then shaking suitably after the addition of water. The formed piece is then fired on schedule to 2400° F. to 2450° F. The useful range of additions is between 1% and 10% of the fluoride, the amount used being to a certain extent dependent on the degree of suppression required. Essentially neutral temperature coefficients are obtained at 2% to 3% addition of MgF_2 and at 4% to 6% addition of CaF_2 .

Example 1

The following compositions were mixed, pressed with the addition of 10% water, dried and then fired to 2450° C. The die size was such that the finished pieces were in the form of discs about 0.85" in diameter and 0.10" in thickness. The opposing parallel faces were silvered and the temperature coefficients determined as described below at 1 megacycle.

Table I

Body No.	Composition	Dielectric constant (20° C.) at 1 megacycle
1	$BaTiO_3$	1,350
2	100 $BaTiO_3$ plus 1 CaF_2	1,220
3	100 $BaTiO_3$ plus 6 CaF_2	1,800
4	100 $BaTiO_3$ plus 10 CaF_2	1,320
5	100 $BaTiO_3$ plus 0.5 MgF_2	1,900
6	100 $BaTiO_3$ plus 1.0 MgF_2	2,580
7	100 $BaTiO_3$ plus 1.5 MgF_2	2,810
8	100 $BaTiO_3$ plus 2.0 MgF_2	3,020
9	100 $BaTiO_3$ plus 2.5 MgF_2	3,400
10	100 $BaTiO_3$ plus 3.0 MgF_2	2,800
11	100 $BaTiO_3$ plus 4.0 MgF_2	2,000
12	100 $BaTiO_3$ plus 5.0 MgF_2	1,100

It should be noted that the addition of a relatively small amount of magnesium fluoride has a profound effect on increasing the dielectric constant of $BaTiO_3$ to approximately twice its nor-

mal level while several percent CaF_2 will increase the dielectric constant about 50%. This advantage in itself is a novel feature entirely outside those recorded above.

In measuring the temperature coefficients of these bodies, pieces roughly 0.85 inch in diameter and 0.10 inch thickness were used and the conventional measurements made in conjunction with a radio frequency bridge of standard make and design. Even though roughly 2 to 2½ hours was the time used in traversing the temperature rise from 20° C. to 150° C. experience indicated that with the particular heating oven used in the tests described herein, a temperature lag of 20° to 30° C. was experienced extending over the entire cycle. Therefore, in order to show the electrical effect obtained, a body made of BaTiO_3 only was measured and these data are included in the tables for comparison purposes. If the data had been obtained over an extremely long time cycle, say 8 to 12 hours, the capacity would have begun to rise precipitously at about 100° C., reaching a peak value at 120° to 130° C. In the present case, in view of the lag known to be present, the peak begins to make itself felt around 120° C. and does not develop nearly so rapidly as when the temperature lag is absent.

Temperature coefficient of dielectric constant is at 1 megacycle per second. Figures are in dielectric constant.

Table II

Temperature, °C.	Body number							
	1	2	3	4	7	8	9	10
20.....	1,350	1,220	1,800	1,320	2,810	3,020	3,400	2,800
30.....	1,350	1,220	1,800	1,330	2,810	3,030	3,400	2,800
40.....	1,338	1,220	1,805	1,330	2,815	3,040	3,310	2,740
50.....	1,330	1,210	1,810	1,330	2,815	3,120	3,210	2,650
60.....	1,329	1,200	1,810	1,350	2,815	3,140	3,050	2,500
70.....	1,321	1,200	1,815	1,360	2,810	3,250	2,880	2,370
80.....	1,312	1,190	1,820	1,360	2,810	3,220	2,630	2,220
90.....	1,312	1,200	1,820	1,360	2,810	3,130	2,410	2,030
100.....	1,316	1,210	1,820	1,350	2,810	2,870	2,180	1,840
110.....	1,340	1,240	1,820	1,300	2,805	2,640	1,945	1,690
120.....	1,378	1,260	1,830	1,220	2,800	2,230	1,720	1,490
130.....	1,426	1,270	1,830	1,100	2,800	2,000	1,480	1,355
150.....	1,685	1,730	1,810	891	2,790	1,690	1,235	1,150

The fluorides of other metals of group II, as for instance, beryllium and strontium, have been found to influence and regulate the dielectric constant of barium titanate but to a somewhat lesser extent than the regulations obtained by calcium or magnesium.

In accordance with the invention therefore, the dielectric constant of barium titanate may be increased by addition of a fluoride of a metal of group II and a composition selected with a suitable temperature coefficient.

What is claimed is:

1. A dielectric material comprising barium titanate in major amount and a fluoride of a metal of group II in minor amount.

2. A dielectric material comprising barium titanate in major amount and calcium fluoride in minor amount.

3. A dielectric material comprising barium titanate in major amount and magnesium fluoride in minor amount.

4. A dielectric material comprising barium titanate and a fluoride of a metal of group II, said metal fluoride being less than 10% of the total composition.

5. A dielectric material comprising barium titanate and calcium fluoride, the calcium fluoride constituting less than 10% of the total composition.

6. A dielectric material comprising barium titanate and magnesium fluoride, the magnesium fluoride constituting less than 10% of the total composition.

7. A dielectric material comprising barium titanate and calcium fluoride, the calcium fluoride constituting from 2% to 5% of the total composition.

8. A dielectric material comprising barium titanate and magnesium fluoride, the magnesium fluoride constituting from 1.5% to 4% of the total composition.

9. The method of regulating the dielectric constant of barium titanate which comprises mixing with barium titanate a fluoride of a metal of group II and heating the mixture until vitrification occurs.

10. The method of regulating the dielectric constant of barium titanate which comprises mixing with barium titanate a fluoride of a metal of group II in an amount less than 10% of the total composition and heating the mixture until vitrification occurs.

11. The method of regulating the dielectric constant of barium titanate which comprises mixing barium titanate and calcium fluoride and heating the mixture until vitrification occurs, the calcium fluoride being less than 10% of the composition.

12. The method of regulating the dielectric constant of barium titanate which comprises mixing barium titanate and magnesium fluoride and heating the mixture until vitrification occurs, the magnesium fluoride being less than 10% of the composition.

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