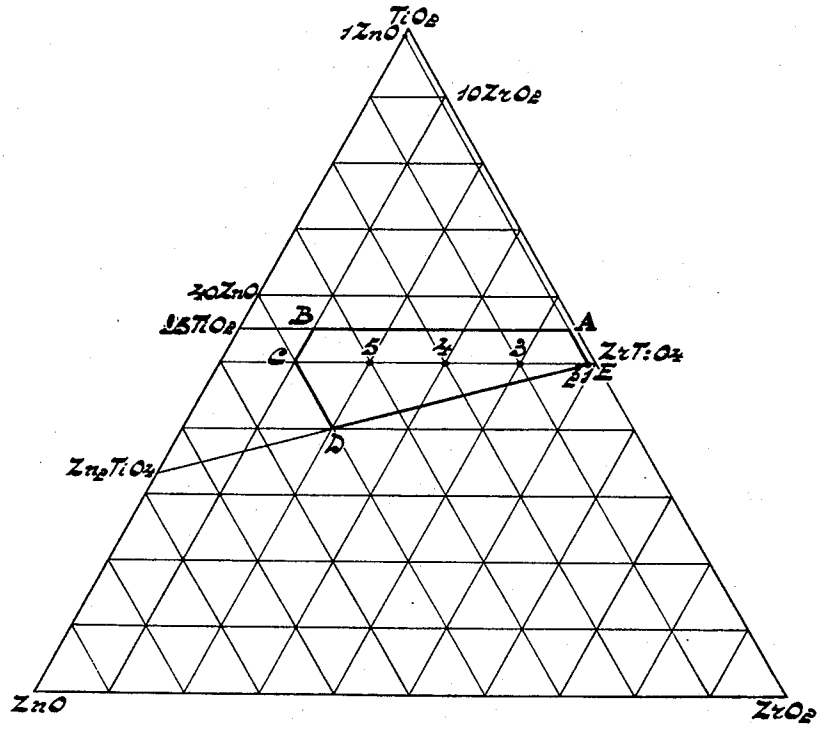
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ELECTRIC INSULATOR

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## ELECTRIC INSULATOR

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7 Claims. (Cl. 106—39)

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The invention relates to ceramic electric insulators having a low temperature coefficient of the dielectric constant, more particularly for use as a capacitor dielectric.

Because titanium dioxide and various titanates have a negative temperature coefficient of the dielectric constant and because most other oxide materials have a positive temperature coefficient, it has been suggested to combine titanium-dioxide or titanates with other oxides, such for example, as magnesium oxide, beryllium oxide, zirconium oxide, tin oxide and cerium oxide, or oxide compounds, such for example, as zirconates and stannates, to act upon the temperature coefficient of ceramic dielectrics. Various of these known combinations have limitations in working, for example, a high sintering temperature or a short sintering period and with others the desired temperature coefficient is only obtained at low values of the dielectric constant. Consequently there is still a need for new means in the art to obtain the aforesaid result.

The invention relates to a ceramic insulator consisting of sintered material, which contains about 1 to 40 mol. per cent oxide, more than 10 mol. per cent zirconium dioxide and titaniumdioxide in a quantity between 33⅓ mol. per cent plus ⅓ of the zirconium dioxide content and 55 mol. per cent. These compositions lie within the pentagon ABCDE, indicated in the ternary diagram $TiO_2$—$ZrO_2$ZnO in the accompanying drawing.

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The products contain a compound of the composition $ZrTiO_4$, which may be termed "zirconiumtitanate." The zirconiumtitanate is a dielectrically very valuable compound which, however, has a limitation in that in its pure state it can be sintered only with difficulty. The material according to the invention, which contains zirconiumtitanate, can, however, be sintered to compactness at temperatures between 1300° and 1500°, in accordance with the zirconiumtitanate content. The temperature coefficient of the dielectric constant lies between $-200.10^{-6}$ and $-10.10^{-6}$ and the dielectric constant between approximately 30 and 45.

The compositions having a titaniumdioxide content of about 50 mol. per cent have the advantage that the value of the dielectric constant ($\epsilon$) is at least 35, the temperature coefficient and the tan $\delta$ having low values. Of some of these compounds, which are indicated in the accompanying drawing by the numerals 1 to 5, the dielectric values and the sintering temperatures are indicated in the Table I:

*Table I*

| No. | ZnO | | $ZrO_2$ | | $TiO_2$ | | $\epsilon$ | Tg. $\delta$ $\times 10^4$ | Temp. Coeff. $\times 10^6$ | Sintering temp. |
|---|---|---|---|---|---|---|---|---|---|---|
| | Mol. percent | Wt. percent | Mol. percent | Wt. percent | Mol. percent | Wt. percent | | | | |
| 1 | 1 | 0.8 | 49.5 | 60.2 | 49.5 | 39.0 | 38 | 0.9 | −114 | 1,500 |
| 2 | 2 | 1.6 | 49 | 59.5 | 49 | 38.9 | 42 | 2.3 | −114 | 1,500 |
| 3 | 10 | 8.1 | 40 | 50 | 50 | 41 9 | 40 | 3.1 | −50 | 1,350 |
| 4 | 20 | 17.3 | 30 | 39.9 | 50 | 42.8 | 34.5 | 10.2 | −91 | 1,300 |
| 5 | 30 | 27.4 | 20 | 27.9 | 50 | 44.7 | 35 | 2.1 | −89 | 1,300 |

A shift of the temperature coefficient in positive sense, though attended with a slight reduction of the dielectric constant, may be obtained by replacing in the aforesaid compositions the titaniumoxide and the zirconiumoxide to such a portion by tin oxide that the tin oxide content of the material is at the most 30 mol. per cent. A few examples thereof are given in Table II.

*Table II*

| No. | ZnO | | $ZrO_2$ | | $TiO_2$ | | $SnO_2$ | | $\epsilon$ | Tg. $\delta$ $\times 10^4$ | Temp. Coeff. $\times 10^6$ | Sint. Temp. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mol. percent | Wt. percent | Mol. percent | Wt. percent | Mol. percent | Wt. percent | Mol. percent | Wt. percent | | | | |
| 6 | 10 | 8 | 30 | 37 | 50 | 40 | 10 | 15 | 40 | 3.9 | −8.8 | 1,360 |
| 7 | 10 | 7.7 | 40 | 47.2 | 40 | 30.7 | 10 | 14.4 | 37 | 3.2 | +5 | 1,360 |
| 8 | 10 | 7.6 | 30 | 34.5 | 40 | 29.7 | 20 | 28.2 | 35 | 3.0 | +47 | 1,360 |
| 9 | 10 | 7.1 | 30 | 32.4 | 30 | 21 | 30 | 39.5 | 31 | 2.1 | +57 | 1,360 |

The titaniumdioxide may furthermore be replaced to such a portion by aluminum oxide that the aluminumoxide content is at the most equal to the zinc oxide content and is maximum 15 mol. per cent. A few examples of such compositions are given in Table III.

*Table III*

| No. | ZnO | | $Al_2O_3$ | | $ZrO_2$ | | $TiO_2$ | | $\epsilon$ | tan $\delta$ × $10^4$ | Temp. coeff. × $10^6$ | Sint. temp. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mol. per-cent | Wt. per-cent | Mol. per-cent | Wt. per-cent | Mol. per-cent | Wt. per-cent | Mol. per-cent | Wt. per-cent | | | | |
| 10 | 11 | 9.2 | 4 | 4.1 | 38 | 48.1 | 47 | 38.6 | 30 | 7.8 | −180 | 1,360 |
| 11 | 14 | 11.7 | 5 | 5.2 | 38 | 48 | 43 | 35.1 | 31 | 8.3 | −43 | 1,360 |
| 12 | 5 | 4 | 5 | 5 | 45 | 55 | 45 | 36 | 33 | 5.0 | −127 | 1,400 |
| 13 | 7.5 | 6.1 | 7.5 | 7.7 | 40 | 49.7 | 45 | 36.5 | 35 | 3.8 | −150 | 1,360 |

If desired, use may be made of sintering or fluxing agents in the manner known in ceramic art in order to reduce the sintering temperature. For this purpose use may, for example, be made of silicates, such as bentonite and fluorides, such as $CaF_2$ and $MgF_2$.

The manufacture of the dielectrics on the basis of zirconiumtitanate according to the invention may be carried out as follows. The oxides, compounds of these oxides or compounds converted into the former by heating are mixed in the aforesaid ratio, if necessary with the addition of a sintering agent and a combustible binder, for example by grinding in a ball mill. The mass is then heated; the temperature may be raised with a speed of, for example, 500° per hour to the sintering temperature; then heating is continued at this temperature for one hour and cooling is effected in two hours.

For use in capacitors the insulators are preferably shaped in the form of tubes and provided with electrodes, for example by applying silver by burning.

What I claim is:

1. A capacitor dielectric consisting of a sintered mass of about 1 to 40 mol. per cent of ZnO, more than 10 mol. per cent of $ZrO_2$, and about 33⅓ mol. per cent plus ⅓ of the $ZrO_2$ content to 55 mol. per cent of $TiO_2$, said product living wholly within a pentagon ABCDE shown in the accompanying drawing of the ternary system $ZrO_2$—ZnO—$TiO_2$.

2. A capacitor dielectric consisting of a sintered mass of about 1 to 40 mol. per cent of ZnO, more than 10 mol. per cent of $ZrO_2$, and about 50 mol. per cent of $TiO_2$, said product lying wholly within a pentagon ABCDE shown in the accompanying drawing of the ternary system $ZrO_2$—ZnO—$TiO_2$.



3. A capacitor dielectric consisting of a sintered mass of about 1 to 40 mol. per cent of ZnO, more than 10 mol. per cent of $ZrO_2$, about 33⅓ mol. per cent plus ⅓ of the $ZrO_2$ content to 55 mol. per cent of $TiO_2$, and up to 30 mol. per cent of $SnO_2$ replacing a corresponding proportion of the $ZrO_2$ and $TiO_2$.

4. A capacitor dielectric consisting of a sintered mass of about 1 to 40 mol. per cent of ZnO, more than 10 mol. per cent of $ZrO_2$, about 33⅓ mol. per cent plus ⅓ of the $ZrO_2$ content to 55 mol. per cent of $TiO_2$, and up to about 15 mol. per cent in $Al_2O_3$ and at most equal to the ZnO content replacing a corresponding amount of the $TiO_2$.

5. A capacitor dielectric consisting of a sintered mass of about 1 to 40 mol. per cent of ZnO, more than 10 mol. per cent of $ZrO_2$, about 33⅓ mol. per cent plus ⅓ of the $ZrO_2$ content to 55 mol. per cent of $TiO_2$, and a fluxing agent.

6. A capacitor dielectric consisting of a sintered mass of about 1 to 40 mol. per cent of ZnO, more than 10 mol. per cent of $ZrO_2$, about 33⅓ mol. per cent plus ⅓ of the $ZrO_2$ content to 55 mol. per cent of $TiO_2$, up to 30 mol. per cent of $SnO_2$ replacing a corresponding proportion of the $ZrO_2$ and $TiO_2$ content and a fluxing agent.

7. A capacitor dielectric consisting of a sintered mass of about 1 to 40 mol. per cent of ZnO, more than 10 mol. per cent of $ZrO_2$, about 33⅓ mol. per cent plus ⅓ of the $ZrO_2$ content to 55 mol. per cent of $TiO_2$, up to about 15 mol. per cent of $Al_2O_3$ and at most equal to the ZnO content replacing a corresponding amount of the $TiO_2$ and a fluxing agent.

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