

NON-REDUCIBLE DIELECTRIC CERAMIC COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a non-reducible dielectric ceramic composition and, more particularly, to a non-reducible dielectric ceramic composition used for monolithic ceramic capacitors.

2. Description of the Prior Art

Monolithic ceramic capacitors are generally produced by first preparing dielectric ceramic green sheets with a dielectric ceramic composition such as a composition mainly comprising barium titanate, applying a conductive material for an internal electrode on one surface of each green sheet, stacking the green sheets, bonding them by thermocompression, cutting the resultant multilayered body into ceramic capacitor green chips, then firing the green chips in air at 1250 - 1350 °C to form capacitor chips with internal electrodes, and finally forming external electrodes connected to the internal electrodes on opposed sides of each of the capacitor chips to complete monolithic ceramic capacitors.

Accordingly, a conductive material for internal electrodes is required to meet conditions such that (a) it has a melting point higher than a sintering temperature of the dielectric ceramics as the internal electrodes are fired

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along with the dielectric ceramic material; and that (b) it neither oxidize nor react with the dielectric ceramics even in an oxidizing atmosphere with a high temperature.

To meet such requirements, noble metals such as platinum, gold, palladium and their alloys have been used as a conductive material for the internal electrodes. Such noble metals provide satisfactory characteristics, but for all practical purposes they are too expensive to use. That is, use of such a noble metal is the greatest factor determining the rise in the production cost of monolithic ceramic capacitors as the cost of internal electrodes occupies from 30 to 70 % of the production cost of monolithic ceramic capacitors.

Other metals having a high melting point are base metals such as Ni, Fe, Co, W and Mo, but they are easily oxidized in a oxidizing high temperature atmosphere. Thus, if such a base metal is used as a material for internal electrodes of monolithic ceramic capacitors, it loses the function serving as the internal electrodes when the green chips are fired in air. It is therefore required to fire the green chips in a neutral or reducing atmosphere in order to use a base metal as a material for internal electrodes of monolithic ceramic capacitors. However, the dielectric ceramic materials of the prior art are reduced considerably and thus semiconductorized when fired in the reducing atmosphere.

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To solve such a problem, it has been proposed in JP-B- 57-42588 to use a dielectric ceramic material comprising a barium titanate solid solution having a ratio of a barium site to a titanium site being larger than the stoichiometric ratio. Such a dielectric ceramic material is scarcely semiconductorized even if fired in a reducing atmosphere, thus making it possible to manufacture monolithic ceramic capacitors including internal electrodes of a base metal such as nickel. It is, however, difficult with such dielectric ceramic materials to miniaturize monolithic ceramic capacitors for the following reasons.

With recent development of electronic techniques, considerable progress has made in miniaturization of electronic devices. Consequently, this requires miniaturization of monolithic ceramic capacitors as well as other electronic parts. For the monolithic ceramic capacitors, the miniaturization is generally carried out by using a dielectric ceramic material with a high dielectric constant or by making dielectric ceramic layers thin. The dielectric ceramic materials as disclosed in JP-B- 57-42588 have high dielectric constant, but they are large in grain size. Thus, if the thickness of dielectric ceramic layers is decreased to 10 μm or below, the number of crystal grains present in each layer is considerably decreased, resulting in lowering of reliability of the monolithic ceramic capacitors.

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On the other hand, JP-B- 61-101459 discloses a nonreducible dielectric ceramic composition consisting of a barium titanate solid solution into which a rare earth element such as La, Nd, Sm and Dy has been incorporated. Such a composition has a fine grain size which enables to avoid lowering of the reliability of monolithic ceramic capacitors as the fine grains size contributes to increase the number of crystal grains present in each dielectric layer. However, it is impossible with such a ceramic composition to obtain high dielectric constant and that the composition containing a rare earth element is easy to oxidize during firing.

SUMMARY OF THE INVENTION

It is therefore a primary object of the present invention to provide a nonreducible dielectric ceramic composition which is large in dielectric constant but small in crystal grain size and which is never semiconductorized even if fired in a reducing atmosphere.

Another object of the present invention is to provide a nonreducible dielectric ceramic composition which enables to miniaturize monolithic ceramic capacitors without lowering of reliability and characteristics.

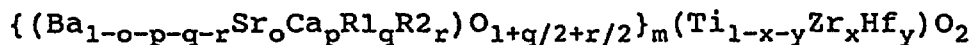
According to the present invention, there is provided a non-reducible dielectric ceramic composition consisting essentially of a main component and at least one additive selected from the group consisting of oxides of Mn,

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Fe, Cr, Co and Ni, said main component having a composition of the general formula (I):



where R1 is at least one element selected from the group consisting of La, Ce, Nd, Pr and Sm R2 is at least one element selected from the group consisting of Dy, Ho, Er, Yb and Y, and o, p, q, r, x, y and m meet the following conditions: $0 < o \leq 0.32$, $0 \leq p \leq 0.20$, $0 < q \leq 0.02$, $0 < r \leq 0.02$, $0 < x \leq 0.24$, $0 < y \leq 0.16$, $1.00 \leq m \leq 1.03$, and $0 < q+r \leq 0.03$; the content of said additive being 0.02 to 2.0 moles per 100 moles of said main component when calculated in terms of respective oxides, MnO, Fe₂O₃, Cr₂O₃, CoO and NiO.

The above composition may contains at least one additional additive selected from the group consisting of SiO₂ and ZnO in an amount of 0.1 to 2.0 moles per 100 moles of the main component.

The above non-reducible dielectric ceramic composition has a small grain size of not more than 3 μm even though it has a high dielectric constant of not less than 11000, thus making it possible to thin the dielectric layers without causing decrease in the number of crystal grains present in each dielectric layer. However, if the contents of R1 and R2 become increased, the dielectric loss becomes more than 1.5% and the insulation resistance becomes lowered. This problem can be solved by addition of a

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certain amount of MgO into the main component.

Thus, according to the present invention there is further provided a non-reducible dielectric ceramic composition consisting essentially of a main component and at least one additive selected from the group consisting of oxides of Mn, Fe, Cr, Co and Ni, said main component having a composition of the general formula (II):

$$(1-a)\{(Ba_{1-o-p-q-r}Sr_oCa_pR1_qR2_r)O_{1+q/2+r/2}\}_m(Ti_{1-x-y}Zr_xHf_y)O_2 + aMgO$$
, where R1 is at least one element selected from the group consisting of La, Ce, Nd, Pr and Sm, R2 is at least one element selected from the group consisting of Dy, Ho, Er, Yb and Y, and a, o, p, q, r, x, y and m meet the following conditions: $0 < a \leq 0.05$, $0 < o \leq 0.32$, $0 \leq p \leq 0.20$, $0 < q \leq 0.02$, $0 < r \leq 0.03$, $0 < x \leq 0.24$, $0 < y \leq 0.16$, $1.00 \leq m \leq 1.03$, and $0 < q+r \leq 0.04$; the content of said additive being 0.02 to 2.0 moles per 100 moles of said main component when calculated in terms of respective oxides, MnO, Fe₂O₃, Cr₂O₃, CoO and NiO.

Also, the composition may contains at least one additional additive selected from the group consisting of SiO₂ and ZnO in an amount of 0.1 to 2.0 moles per 100 moles of the main component.

The dielectric ceramic composition of the present invention is never reduced or semiconductorized even if fired in a reducing atmosphere. Furthermore, the dielectric ceramic composition of the present invention can be fired at

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a temperature of not more than 1300 °C. Accordingly, the non-reducible dielectric ceramic composition of the present invention makes it possible to use any base metal as a material for internal electrodes of monolithic ceramic capacitors, which in turn makes it possible to cut down the production cost of monolithic ceramic capacitors.

The non-reducible dielectric ceramic composition of the present invention has a small grain size of not more than 3 μm though it has a high dielectric constant of not less than 9000, thus making it possible to thin the dielectric layers without causing decrease in the number of crystal grains present in each dielectric layer. Thus, the present invention makes it possible to manufacture monolithic ceramic capacitors which have high reliability and which are small in size but large in capacitance.

The above and other objects, features and advantages of the present invention will become apparent from the following examples.

EXAMPLE 1

Using, as raw materials, BaCO_3 , SrCO_3 , CaCO_3 , CeO_2 , La_2O_3 , Nd_2O_3 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Yb_2O_3 , Y_2O_3 , TiO_2 , ZrO_2 , HfO_2 , MnO , Fe_2O_3 , Cr_2O_3 , CoO and NiO with the purity of not less than 99.8%, there were prepared specimens of dielectric ceramic compositions in the following manner:

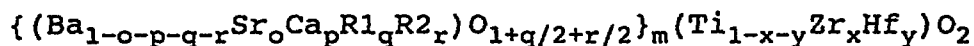
Firstly, the raw materials, BaCO_3 , SrCO_3 , CaCO_3 , CeO_2 , La_2O_3 , Nd_2O_3 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Yb_2O_3 , Y_2O_3 , TiO_2 ,

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ZrO₂ and HfO₂, were weighed and mixed to prepare a mixture for a main component having a composition expressed by the general formula (I):



with values of o, p, q, r, m, x and y shown in Table 1. The remaining raw materials, MnO, Fe₂O₃, Cr₂O₃, CoO and NiO, were added as an additive to the resultant mixture in proportions shown in Table 1 in which the added amounts of the additive are listed in mole per 100 moles of the main component, respectively.

The resultant mixture was wet-milled with a ball mill for 16 hours, dried by evaporation, calcined in air at 1100 °C for 2 hours, and then crushed and pulverized by a dry grinding machine to prepare a calcined powder with a particle size of 1 μm or smaller.

The calcined powder was added with suitable amounts of pure water and an organic binder of polyvinyl acetate, and wet-milled for 16 hours with a ball mill and then granulated to prepare molding powder. The powder was then molded under a pressure of 2000 Kg/cm² to prepare green compacts of a diameter of 10 mm and a thickness of 0.5 mm. The green compacts were heated to 500 °C in air to remove the organic binder by combustion, and then fired at a temperature shown in Table 2 for 2 hours in a reducing atmosphere consisting of H₂, N₂ and air with a partial pressure of oxygen being 2 x 10⁻¹⁰ to 3 x 10⁻¹² atm to

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prepare ceramic disks.

The resultant ceramic disks were observed by a scanning-electron microscope at a magnification of 1500 to determine crystal grain size.

Each ceramic disk was provided on its opposite sides with silver electrodes by applying a silver paste and then baking it at 600 °C for 30 minutes in a nitrogen atmosphere to prepare a capacitor to be used as a specimen for measurements of electrical properties.

For each specimen, measurements were made on dielectric constant (ϵ), dielectric loss ($\tan \delta$), and a temperature coefficient (TC) of capacitance (C), and insulation resistance. The dielectric constant and dielectric loss were measured at 1 kHz, 1 Vrms at 25°C. The temperature coefficient (TC) of capacitance was determined over the temperature range of -25°C to 85°C on the basis of the capacitance at 20°C along with the largest absolute value of TC in the range of -25°C to 85°C. The temperature coefficient (TC) of capacitance was given by equation: $TC = \Delta C / C_{20}$, where ΔC is difference between capacitance at the measured temperature and that at 20°C, and C_{20} is a capacitance at 20 °C.

The insulation resistance was measured at 25 °C and 85 °C after applying a direct voltage of 500 V to the specimen for 2 minutes. The results are shown in Table 2 in which the insulation resistance is given as a logarithmic

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value of volume resistance ($\log \rho$).

In Table 1 and Table 2, specimens with an asterisk are those having a composition out of the scope of the present invention.

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Table 1

No	Main component $\{(Ba_{1-o-p-q-r}Sr_oCa_pRl_qR2_r)O_{1+q/2+r/2}\}_m(Ti_{1-x-y}Zr_xHf_y)O_2$								Additive(mol)				
	o	p	q	r	q+r	m	x	y	MnO	Fe ₂ O ₃	Cr ₂ O ₃	CoO	NiO
*1	0	0.05	Ce:0.005	Y:0.0075	0.0125	1.007	0.06	0.02	0.3	-	-	-	-
*2	0.15	0.08	-	Y:0.005	0.005	1.007	0.09	0.01	0.3	-	-	-	0.2
*3	0.08	0.05	Ce:0.005	-	0.005	1.007	0.06	0.02	0.3	-	-	-	0.1
*4	0.18	0.03	Ce:0.005	Y:0.0075	0.0125	1.005	0	0.03	0.3	-	-	-	0.1
*5	0.10	0.10	Ce:0.005	Y:0.0075	0.0125	1.005	0.08	0	0.3	-	-	-	-
*6	0.06	0.03	Ce:0.005	Y:0.0075	0.0125	1.005	0.10	0.02	-	-	-	-	-
*7	0.06	0.03	Ce:0.005	Y:0.0075	0.0125	0.995	0.10	0.02	0.3	-	-	-	0.1
8	0.01	0.03	Ce:0.005	Y:0.0075	0.0125	1.007	0.13	0.005	0.3	-	-	-	0.2
9	0.01	0	La:0.001 Nd:0.003	Y:0.008	0.012	1.01	0.12	0.01	0.4	-	-	-	0.1
10	0.08	0.02	Ce:0.005	Dy:0.007	0.012	1.007	0.11	0.01	0.3	-	0.1	-	0.2
11	0.14	0.02	Ce:0.001	Dy:0.01 Er:0.005 Y:0.005	0.021	1.01	0.04	0.05	0.3	-	-	-	0.2
12	0.32	0.05	Ce:0.0025	Er:0.01	0.0125	1.007	0.05	0.005	0.3	0.1	-	-	0.2
13	0.05	0.20	Ce:0.004	Ho:0.002 Yb:0.006	0.012	1.01	0.01	0.16	0.02	-	-	-	-

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Table 1(continued)

No.	Main component $\{(Ba_{1-o-p-q-r}Sr_oCa_pRl_qR2_r)O_{1+q/2+r/2}\}_m(Ti_{1-x-y}Zr_xHf_y)O_2$								Additive(mol)				
	o	p	q	r	q+r	m	x	y	MnO	Fe ₂ O ₃	Cr ₂ O ₃	CoO	NiO
14	0.04	0.10	La:0.005 Ce:0.01 Nd:0.005	Y:0.01	0.03	1.03	0.07	0.01	1.0	0.2	-	0.4	0.4
15	0.06	0.02	Ce:0.005	Y:0.007	0.012	1.01	0.13	0.01	0.3	-	-	-	0.1
16	0.03	0.02	Ce:0.001	Y:0.001	0.002	1.00	0.24	0.001	0.3	-	-	-	-
17	0.01	0	Ce:0.0025	Y:0.005	0.0075	1.015	0.15	0.001	0.4	-	-	0.05	0.05
*18	0.38	0.01	Ce:0.005	Y:0.007	0.012	1.005	0.14	0.01	0.3	-	-	-	0.1
*19	0.03	0.25	Ce:0.002	Y:0.005	0.007	1.005	0.15	0.005	0.3	-	-	-	0.1
*20	0.06	0.02	Ce:0.025	Dy:0.003	0.028	1.005	0.12	0.01	0.3	-	-	-	0.1
*21	0.06	0.02	Ce:0.005	Y:0.025	0.03	1.005	0.12	0.01	0.3	-	-	-	0.1
*22	0.06	0.02	Ce:0.02	Y:0.02	0.04	1.007	0.12	0.01	0.3	-	-	-	-
*23	0.06	0.02	Ce:0.005	Y:0.005	0.01	1.007	0.30	0.005	0.3	-	-	-	-
*24	0.06	0.02	Ce:0.005	Y:0.005	0.01	1.007	0.05	0.20	0.3	-	-	-	-
*25	0.06	0.02	Ce:0.005	Y:0.007	0.012	1.007	0.13	0.01	3.0	-	-	-	0.1
*26	0.06	0.02	Ce:0.005	Y:0.007	0.012	1.05	0.13	0.01	0.3	-	-	-	0.1

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Table 2

No	firing temp. (°C)	ϵ	$\tan \delta$ (%)	TC of capacitance $\Delta C/C_{20}(\%)$			Volume resistance $\log \rho (\Omega \cdot \text{cm})$		grain size (μm)
				-25°C	85°C	$ \Delta C/C_{20} _{\text{max}}$	25°C	85°C	
*1	1280	5800	2.5	-51	15	96	13.0	12.7	2.0
*2	1280	11200	1.2	-70	-65	70	13.2	12.7	4.0
*3	1280	7300	2.1	-62	-10	81	13.0	12.9	2.7
*4	1280	7000	1.6	-67	30	120	12.9	12.8	2.5
*5	1280	6500	1.8	-63	-15	73	13.1	13.0	2.5
*6	1280	12100	1.2	-70	-73	73	12.0	8.2	2.2
*7	1280	Unmeasurable					6.1	5.5	2.7
8	1280	12200	1.3	-74	-67	74	13.0	12.8	2.0
9	1260	13300	1.1	-72	-70	72	13.1	12.8	2.2
10	1280	13600	0.6	-70	-73	73	13.0	12.9	2.5
11	1280	12400	0.4	-73	-65	73	12.9	12.7	2.5
12	1280	12900	0.4	-71	-74	74	13.0	12.9	2.7
13	1300	11300	0.7	-58	-42	58	13.0	12.4	2.0

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Table 2 (continued)

No	firing temp. (°C)	ε	tan δ (%)	TC of capacitance ΔC/C ₂₀ (%)			Volume resistance log ρ (Ω·cm)		grain size (μm)
				-25°C	85°C	ΔC/C ₂₀ _{max}	25°C	85°C	
14	1280	12300	1.5	-76	-72	76	12.6	12.1	2.0
15	1260	13700	0.9	-72	-75	75	13.1	13.0	2.2
16	1300	11100	0.2	-47	-65	65	13.2	12.9	3.0
17	1280	11700	0.4	-70	-73	73	13.1	13.0	3.0
*18	1280	6700	0.1	32	70	70	13.3	13.0	3.0
*19	1340	5500	0.5	-37	-46	46	13.3	13.1	3.0
*20	1280	15100	3.1	-59	-70	70	8.2	7.0	2.0
*21	1280	11500	2.3	-53	-73	73	9.2	7.5	2.5
*22	1280	Unmeasurable					6.0	5.6	2.0
*23	1340	4300	0.08	10	-59	59	13.0	12.8	2.5
*24	1280	16000	0.3	-71	-82	82	13.0	12.7	3.0
*25	1280	12800	2.3	-70	-75	75	11.5	8.0	3.5
*26	Insufficiently sintered								0.2

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As can be seen from the above results, the non-reducible dielectric ceramic composition of the present invention possesses a high dielectric constant equal to or more than 11000, a low loss tangent of equal to or less than 2.0 %, and good temperature coefficient of capacitance which meets requirements of F characteristics defined by Japanese Industrial Standard (JIS) in the temperature range of -25 °C to +85°C.

In addition, the composition of the present invention possesses a high value of the insulation resistance of which a logarithmic value is equal to or more than 12. Further, the composition can be sintered at a relatively low temperature of not more than 1300 °C and has a small grain size of 3 μm or below which makes it possible to thin the dielectric layers of the monolithic ceramic capacitors.

The main component of the non-reducible dielectric ceramic composition has been limited to those having a composition expressed by the general formula (I) for the following reasons:

If the molar fraction of Sr, x , is 0, like as specimen No. 1, the dielectric constant becomes less than 11000, the dielectric loss exceeds 2.0 % and the temperature coefficient of capacitance becomes large. If x exceeds 0.32, like as specimen No. 18, the dielectric constant becomes less than 11000 and the temperature coefficient of



capacitance becomes large and does not meet the requirements of F characteristics defined by JIS.

If the molar fraction of Ca, p, exceeds 0.20, like as specimen No. 19, the sintering properties of the dielectric ceramic composition become worse.

If the molar fraction of R1, q, is 0, like as specimen No. 2, the crystal grain size exceeds 3 μm , which in turn makes it impossible to thin the dielectric layers for monolithic ceramic capacitors. If q exceeds 0.02, like as specimen No. 20, the dielectric loss exceeds 2.0 % and the insulation resistance at 25°C or 85°C becomes lowered.

If the molar fraction of R2, r, is 0, like as specimen No. 3, the dielectric constant becomes less than 11000 and the temperature coefficient of capacitance becomes large. If r exceeds 0.02, like as specimen No. 21, the dielectric loss exceeds 2.0 % and the insulation resistance becomes lowered.

If the sum of the molar fractions of R1 and R2, i.e., q+r, exceeds 0.03, like as specimen No. 22, the composition is reduced and semiconductorized when fired in a reducing atmosphere, whereby the insulation resistance becomes considerably lowered.

If the molar fraction of Zr, x, is 0, like as specimen No. 4, the dielectric constant becomes less than 11000 and the temperature coefficient of capacitance becomes large. If x exceeds 0.24, like as specimen No. 23, the



sintering properties become lowered and the dielectric constant becomes less than 11000.

If the molar fraction of Hf, y , is 0 like as specimen No. 5, the dielectric constant becomes less than 11000. if y exceeds 0.16, like as specimen No. 24, the temperature coefficient of capacitance does not meet the requirements of F characteristics defined by JIS.

If the molar ratio of $\{(Ba_{1-o-p-q-r}Sr_oCa_pR1_qR2_r)O_{1+q/2+r/2}\}$ to $(Ti_{1-x-y}Zr_xHf_y)O_2$, i.e., m , is less than 1.00 like as specimen No. 7, the insulation resistance becomes lowered as the composition is reduced and semiconductorized when fired in a reducing atmosphere. On the other hand, if m exceeds 1.03, like as specimen No. 26, the sintering properties becomes considerably lowered. Thus, the molar ratio of the barium site to titanium site has been limited to a value ranging from 1.000 to 1.03.

Further, if the added amount of the additive, MnO , Fe_2O_3 , Cr_2O_3 , CoO and NiO , is less than 0.02 mole per 100 mole of the main component, like as specimen No. 6, the insulation resistance at 85°C and above becomes small, resulting in lowering of the reliability in a long use at high temperatures. If the added amount of the above additive exceeds 2.0 moles per 100 mole of the main component, like as specimen No. 25, the dielectric loss exceeds 2.0 % and the insulation resistance becomes lowered. For these reasons, the added amount of the additive has been



limited to a value ranging from 0.02 to 2.0 moles per 100 moles of the main component.

EXAMPLE 2

Using calcined powders of specimen Nos. 2, 3, 15 and 17 prepared in Example 1 for and having particle size of not more than 1 μm , there were prepared monolithic ceramic capacitors in the following manner.

Separate from the above, using, as raw materials, BaCO_3 , SrCO_3 , CaCO_3 , TiO_2 , ZrO_2 , HfO_2 , MnO and NiO with the purity of not less than 99.8%, there was prepared a calcined powder for comparative specimen No. 27 in the following manner: The raw materials were weighed and mixed so that the resultant product has a composition of 100 mol $\{(\text{Ba}_{0.92}\text{Sr}_{0.06}\text{Ca}_{0.02})\text{O}\}_{1.01}(\text{Ti}_{0.83}\text{Zr}_{0.16}\text{Hf}_{0.01})\text{O}_2 + 0.3 \text{ mol MnO} + 0.1 \text{ mol NiO}$. The resultant mixture of the raw materials was wet-milled with a ball mill for 16 hours, dried by evaporation, calcined in air at 1100 °C for 2 hours, and then crushed and pulverized by a dry grinding machine to prepare a calcined powder with a particle size of 1 μm or below.

Each calcined powder was wet-milled with a ball mill for 16 hours together with a suitable amount of polyvinyl butyral resin dissolved in ethyl alcohol to prepare a ceramic slurry. Then, the slurry was formed into a sheet by the Doctor blade process, dried and then cut to prepare ceramic green sheets with a thickness of 18 μm .



A conductive paste containing Ni as a conductive material was screen-printed on one surface of each ceramic green sheet to form a conductive paste layer for internal electrodes. Subsequently, 19 sheets of the resultant printed green sheets were stacked, bonded by thermo-compression along with two non-printed green sheets put on the opposite surfaces of the stack, and then cut into pieces to form green chips for monolithic ceramic capacitors. The green chips were fired with an electric furnace at 350°C in a nitrogen atmosphere to burn the binder, and then fired at a temperature shown in Table 3 for 2 hours in a reducing atmosphere composed of a mixed gas of N₂, H₂ and air with a partial pressure of oxygen being 2×10^{-10} to 3×10^{-12} atm to prepare monolithic ceramic capacitor chips.

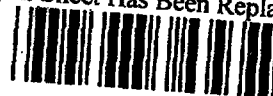
The resultant capacitor chips were observed by a scanning-electron microscope at a magnification of 1500 to determine crystal grain size.

The capacitor chips were provided on its opposite sides with external electrodes connected to internal electrodes by applying a silver paste and then baking it at 600 °C for 30 minutes in a nitrogen atmosphere to produce a monolithic ceramic capacitor.

The thus prepared monolithic ceramic capacitors have the following dimensions and constituents:

Width: 1.6 mm

Length: 3.2 mm



Thickness: 1.2 mm

Thickness of each dielectric layer: 15 μm .

Number of effective dielectric layers: 19 sheets

Surface area of internal electrode: 2.1 mm²

Dielectric constant (ϵ) and dielectric loss ($\tan \delta$) were measured at 1 kHz, 1 Vrms at 25°C. The insulation resistance (R) was measured at 25 °C and 85 °C after applying a direct voltage of 16 V to the specimen for 2 minutes. The results are shown in Table 3 in which the insulation resistance is given as the product of insulation resistance and capacitance (CR).

The temperature coefficient (TC) of capacitance was determined over the temperature range of -25°C to 85°C on the basis of the capacitance at 20°C along with the largest absolute value of TC in the range of -25°C to 85°C. The temperature coefficient (TC) of capacitance was given by equation: $TC = \Delta C / C_{20}$, where ΔC is difference between capacitance at the measured temperature and that at 20°C, and C_{20} is a capacitance at 20 °C.

A high temperature load life test was carried out by applying DC voltage of 150 volts to the specimen at 150°C. The specimen, i.e., a capacitor, was considered to be failed when the insulation resistance fell below $10^6 \Omega$. The high temperature load life time is given as a mean value of data for 36 chips.

The capacitance of each specimen was measured

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before and after a high temperature load test which was carried out by applying a DC voltage of 32 volts to the specimen at 85°C for 1000 hours. From the data, a change rate of capacitance was determined by the equation: $(\Delta C' / C_0) \times 100$, where $\Delta C' = C_{1000} - C_0$, C_{1000} is a capacitance measured after the test, C_0 is a capacitance measured before the test.

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Table 3

No.	Firing temp. (°C)	ϵ	tan δ (%)	$\Delta C/C_{20}^{\circ C}(\%)$		CR (M $\Omega \cdot \mu F$)		mean life time(h)	$\Delta C'/C_0$ (%)	grain size (μm)
				-25°C	85°C	25°C	85°C			
*2	1270	16500	3.9	-58	-76	20,600	11,100	38	-4	3.7
*3	1270	10800	8.7	-50	-62	18,900	10,700	140	-17	2.4
15	1270	17200	3.7	-55	-78	29,700	15,800	172	-4	2.8
17	1270	15800	3.3	-44	-77	21,300	14,400	147	-3	3.0
*27	1270	15100	4.0	-41	-80	19,300	12,000	6	-20	4.2

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As can be seen from the results shown in Table 3, the monolithic ceramic capacitors including the non-reducible dielectric ceramic composition of the present invention are high in dielectric constant, small in dielectric loss ($\tan \delta$) and possess good temperature characteristics as the temperature coefficient of capacitance ($\Delta C/C_{20}$) meets requirements of F characteristics defined by JIS in the temperature range of -25°C to $+85^{\circ}\text{C}$. In addition, the composition of the present invention has an high insulation resistance as the product of C and R is more than $10000 \text{ M}\Omega \cdot \mu\text{F}$ at 25°C and more than $5000 \text{ M}\Omega \cdot \mu\text{F}$ at 85°C . Further, the composition has a long high temperature life time of more than 100 hours and the change rate of capacitance under the high temperature load test is less than 10 %.

In contrast therewith, the specimen No. 2 containing no element R1 selected from the group consisting of La, Ce, Nd is short in high temperature life time. The specimen No. 3 containing no element R2 selected from the group consisting of Dy, Ho, Er, Yb and Y is low in dielectric constant, but large in dielectric loss. In addition, the change rate of capacitance become large when the capacitor is subjected to the high temperature load test for 1000 hours.

The specimen containing no element of R1 and R2 is short in high temperature life time, but large in change

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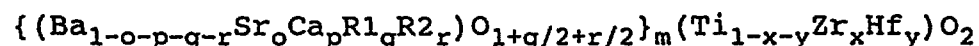
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rate of capacitance. Thus, it can be seen that the co-addition of R1 and R2 contributes to improve both the high temperature life time and the change rate of capacitance due to aging during load life test.

EXAMPLE 3

Using, as raw materials, BaCO_3 , SrCO_3 , CaCO_3 , CeO_2 , La_2O_3 , Nd_2O_3 , Pr_6O_{11} , Sm_2O_3 , DY_2O_3 , Ho_2O_3 , Er_2O_3 , Yb_2O_3 , Y_2O_3 , TiO_2 , ZrO_2 , HfO_2 , MgO , MnO , Fe_2O_3 , Cr_2O_3 , CoO and NiO with the purity of not less than 99.8%, there were prepared specimens of dielectric ceramic compositions in the following manner:

The raw materials, BaCO_3 , SrCO_3 , CaCO_3 , CeO_2 , La_2O_3 , Nd_2O_3 , Pr_6O_{11} , Sm_2O_3 , DY_2O_3 , Ho_2O_3 , Er_2O_3 , Yb_2O_3 , Y_2O_3 , TiO_2 , ZrO_2 and HfO_2 , were weighed and mixed to prepare a mixture for a basic composition for a main component, of the formula (III):



with a set of o, p, q, r, m, x and y shown in Table 4.

The resultant mixture of the raw materials was wet-milled with a ball mill for 16 hours, dried by evaporation, calcined in air at 1100 °C for 2 hours, and then pulverized by a dry grinding machine to prepare a calcined powder with a particle size of 1 μm or below.

Added to 100 moles of the calcined power was the remaining raw materials MgO , MnO , Fe_2O_3 , Cr_2O_3 , CoO and NiO . The added amounts of additives are shown in Table 5. Then,

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the resultant mixture was added with suitable amounts of pure water and an organic binder of polyvinyl acetate, wet-milled for 16 hours with a ball mill and then granulated to prepare molding powder. The powder was then molded under a pressure of 2000 Kg/cm² to prepare green compacts of a diameter of 10 mm and a thickness of 0.5 mm. The green compacts were heated to 500 °C in air to remove the organic binder by combustion, and then fired at a temperature shown in Table 6 for 2 hours in a reducing atmosphere consisting of H₂, N₂ and air with a partial pressure of oxygen being 2×10^{-10} to 3×10^{-12} atm to prepare ceramic disks.

The resultant ceramic disks were observed by a scanning-electron microscope at a magnification of 1500 to determine crystal grain size.

Each ceramic disk was provided on its opposite sides with silver electrodes by applying a silver paste and then baking it at 600 °C for 30 minutes in a nitrogen atmosphere to prepare a capacitor to be used as a specimen for measurements of electrical properties.

For each specimen, measurements were made on dielectric constant (ϵ), dielectric loss ($\tan \delta$), and a temperature coefficient (TC) of capacitance (C), and insulation resistance. The dielectric constant and dielectric loss were measured at 1 kHz, 1 Vrms at 25 °C. The temperature coefficient (TC) of capacitance was determined over the temperature range of -25°C to 85°C on

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the basis of the capacitance at 20°C along with the largest absolute value of TC in the range of -25°C to 85°C. The temperature coefficient (TC) of capacitance was given by equation: $TC = \Delta C / C_{20}$, where ΔC is difference between capacitance at the measured temperature and that at 20°C, and C_{20} is a capacitance at 20 °C.

The insulation resistance was measured at 25 °C and 85 °C after applying a direct voltage of 500 V to the specimen for 2 minutes. The results are shown in Table 6 in which the insulation resistance is given as a logarithmic value of volume resistance ($\log \delta$).

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Table 4

No.	Basic composition for main component $\{(Ba_{1-o-p-q-r}Sr_oCa_pRl_qR2_r)O_{1+q/2+r/2}\}_m(Ti_{1-x-y}Zr_xHf_y)O_2$							
	o	p	q	r	q+r	m	x	y
*28	0	0.02	Ce:0.005	Dy:0.0075	0.0125	1.005	0.06	0.02
*29	0.15	0.02	-	Dy:0.005	0.005	1.003	0.11	0.01
*30	0.08	0.05	Ce:0.005	-	0.005	1.003	0.06	0.02
*31	0.18	0.02	Ce:0.005	Dy:0.005	0.010	1.003	0	0.03
*32	0.10	0.10	Ce:0.005	Dy:0.075	0.0125	1.003	0.08	0
*33	0.05	0.02	Ce:0.005	Dy:0.030	0.035	1.003	0.05	0.005
*34	0.05	0.02	Ce:0.005	Dy:0.005	0.010	1.005	0.12	0.02
*35	0.05	0.02	Ce:0.005	Dy:0.005	0.010	0.99	0.12	0.02
36	0.05	0.02	Ce:0.005	Dy:0.003	0.008	1.004	0.14	0.005
37	0.005	0	Ce:0.001	Dy:0.001	0.002	1.00	0.24	0.001
38	0.15	0.05	Sm:0.002	Yb:0.006	0.008	1.003	0.11	0.005
39	0.32	0.01	La:0.001	Y:0.03	0.031	1.003	0.05	0.001
40	0.01	0.10	La:0.002	Dy:0.003 Ho:0.002	0.007	1.004	0.12	0.005

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Table 4 (continued)

No.	Basic composition for main component $\{(Ba_{1-o-p-q-r}Sr_oCa_pRl_qR2_r)O_{1+q/2+r/2}\}_m(Ti_{1-x-y}Zr_xHf_y)O_2$							
	o	p	q	r	q+r	m	x	y
41	0.01	0.20	Nd:0.002	Yb:0.002	0.004	1.004	0.01	0.16
42	0.002	0.08	La:0.01 Nd:0.006 Pr:0.004	Er:0.02	0.04	1.03	0.05	0.005
43	0.03	0.02	Ce:0.01	Y:0.01	0.02	1.002	0.05	0.07
44	0.01	0	Sm:0.005	Er:0.005	0.01	1.003	0.17	0.01
*45	0.38	0.01	Ce:0.005	Dy:0.005	0.01	1.003	0.13	0.02
*46	0.03	0.25	Ce:0.002	Dy:0.008	0.01	1.005	0.12	0.01
*47	0.05	0.02	Ce:0.025	Er:0.01	0.035	1.003	0.13	0.01
*48	0.05	0.02	Ce:0.005	Dy:0.035	0.04	1.003	0.13	0.01
*49	0.05	0.02	Ce:0.02	Dy:0.03	0.05	1.003	0.13	0.01
*50	0.05	0.02	Ce:0.005	Dy:0.005	0.01	1.003	0.30	0.005
*51	0.05	0.02	Ce:0.005	Dy:0.005	0.01	1.003	0.05	0.20
*52	0.05	0.02	Ce:0.005	Dy:0.005	0.01	1.003	0.13	0.01
*53	0.05	0.02	Ce:0.005	Dy:0.005	0.01	1.003	0.12	0.01
*54	0.05	0.02	Ce:0.005	Dy:0.005	0.01	1.05	0.13	0.01

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Table 5

No	a	Additive (mol)				
		MnO	Fe ₂ O ₃	Cr ₂ O ₃	CoO	NiO
*28	0.005	0.4	-	-	-	-
*29	0.005	0.4	-	-	-	-
*30	0.005	0.3	-	-	0.1	-
*31	0.01	0.4	-	-	-	-
*32	0.01	0.3	-	-	0.1	-
*33	0	0.3	-	-	0.1	-
*34	0.005	-	-	-	-	-
*35	0.005	0.4	-	-	-	-
36	0.005	0.4	-	-	-	0.1
37	0.005	0.3	-	-	-	-
38	0.005	0.3	-	-	-	0.2
39	0.005	0.3	-	-	-	-
40	0.02	0.4	-	-	-	-
41	0.001	0.02	-	-	-	-
42	0.01	1.0	0.1	-	0.7	0.2
43	0.05	0.2	-	-	0.1	-
44	0.005	0.3	-	-	-	-
*45	0.005	0.3	-	-	0.1	-
*46	0.005	0.3	-	-	0.1	-
*47	0.005	0.3	-	-	0.1	-
*48	0.005	0.3	-	-	0.1	-
*49	0.005	0.3	-	-	-	0.1
*50	0.005	0.3	-	-	-	-
*51	0.005	0.3	-	-	-	-
*52	0.08	0.3	-	-	-	0.1
*53	0.005	3.0	-	-	0.1	-
*54	0.005	0.3	-	-	0.1	-

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Table 6

No.	firing temp. (°C)	ϵ	tan δ (%)	TC of capacitance $\Delta C/C_{20}(\%)$			log ρ ($\Omega \cdot \text{cm}$)		grain size (μm)
				-25°C	85°C	$ \Delta C/C_{20} _{\text{max}}$	25°C	85°C	
*28	1280	5800	2.3	-47	17	83	13.1	12.7	2.5
*29	1280	10800	1.5	-69	-64	69	13.3	12.7	4.2
*30	1280	6900	1.9	-60	-15	83	13.0	12.9	2.2
*31	1280	6600	1.5	-63	17	95	13.0	12.8	2.2
*32	1280	5900	1.8	-58	-10	68	13.1	13.0	2.5
*33	1280	14300	2.9	-75	-64	75	9.7	7.8	2.5
*34	1300	11700	1.4	-72	-67	72	12.1	8.5	2.2
35	1280	Unmeasurable							3.0
36	1280	13300	0.8	-67	-73	73	13.2	13.0	2.5
37	1280	9700	0.4	-38	-54	54	13.2	12.8	3.0
38	1280	12500	0.8	-71	-65	71	13.0	13.0	2.5
39	1300	13000	1.0	-70	-73	73	13.0	12.9	2.5
40	1280	9200	0.6	-42	-52	52	13.3	13.1	2.5
41	1300	11000	0.7	-57	-40	57	13.1	13.0	2.0
42	1300	11400	1.4	-60	-68	68	12.6	12.4	2.2

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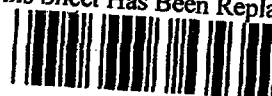
Table 6(continued)

No.	firing temp. (°C)	ϵ	$\tan \delta$ (%)	TC of capacitance $\Delta C/C_{20}$ (%)			Volume resistance $\log \rho (\Omega \cdot \text{cm})$		grain size (μm)
				-25°C	85°C	$ \Delta C/C_{20} _{\text{max}}$	25°C	85°C	
43	1280	10100	0.6	-57	-65	65	13.0	12.9	2.0
44	1260	15700	0.7	-65	-74	74	13.2	13.0	3.0
*45	1280	4900	0.09	41	-59	59	13.0	12.8	3.0
*46	1350	5100	0.6	-12	-48	48	13.1	12.8	3.0
*47	1280	14500	3.0	-45	-70	70	9.0	7.7	2.0
*48	1280	12600	2.4	-40	-71	71	10.1	7.7	2.5
*49	1280	Unmeasurable							2.2
*50	1350	3200	0.06	7	-50	50	13.0	12.8	2.2
*51	1280	16200	0.4	-72	-81	81	13.1	12.6	3.0
*52	1350	4500	0.4	10	-44	44	12.8	12.5	1.5
*53	1280	12700	2.6	-72	-70	72	11.1	8.3	3.5
*54	Insufficiently sintered								

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As can be seen from the above results, if the molar fraction of Sr, o , is 0, like as specimen No. 28, the dielectric constant becomes less than 9000, the dielectric loss exceeds 1.5 % and the temperature coefficient of capacitance becomes large. If o exceeds 0.32, like as specimen No. 45, the dielectric constant becomes less than 9000 and the temperature coefficient of capacitance becomes large and does not meet the requirements of F characteristics defined by JIS.

If the molar fraction of Ca, p , exceeds 0.20, like as specimen No. 46, the sintering properties become worse and the dielectric constant becomes lowered.

If the molar fraction of R1, q , is 0, like as specimen No. 29, the crystal grain size exceeds 3 μm , thus making it impossible to thin the dielectric layers when producing monolithic ceramic capacitors. If q exceeds 0.02, like as specimen No. 47, the dielectric loss exceeds 1.5 % and the insulation resistance at 25°C or 85°C becomes lowered.

If the molar fraction of R2, r , is 0, like as specimen No. 30, the dielectric constant becomes less than 9000 and the temperature coefficient of capacitance becomes large. If r exceeds 0.03, like as specimen No. 48, the dielectric loss exceeds 1.5% and the insulation resistance becomes lowered.

If the sum of the molar fractions of R1 and R2,

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i.e., $q+r$, exceeds 0.04, like as specimen No. 49, the composition is reduced and semiconductorized when fired in a reducing atmosphere, whereby the insulation resistance becomes considerably lowered.

If the molar fraction of Zr, x , is 0, like as specimen No. 31, the dielectric constant becomes less than 9000 and the temperature coefficient of capacitance becomes large. If x exceeds 0.24, like as specimen No. 50, the sintering properties become lowered and the dielectric constant becomes less than 9000.

If the molar fraction of Hf, y , is 0, like as specimen No. 32, the dielectric constant becomes less than 9000. if y exceeds 0.16, like as specimen No. 51, the temperature coefficient of capacitance does not meet the requirements of F characteristics defined by JIS.

If the content of MgO is 0, like as specimen No. 33, the dielectric loss is increased to more than 1.5 by the addition of R1 and R2 exceeding 0.03, and the insulation resistance becomes lowered. If the molar fraction of MgO exceeds 0.05, like as specimen No. 52, the sintering properties becomes lowered and the dielectric constant becomes less than 9000.

If the molar ratio of $\{(Ba_{1-o-p-q-r}Sr_oCa_pR1_qR2_r)O_{1+q/2+r/2}\}$ to $(Ti_{1-x-y}Zr_xHf_y)O_2$, i.e., m , is less than 1.00, like as specimen No. 35, the insulation resistance becomes lowered as the composition is reduced and



semiconductorized when fired in a reducing atmosphere. If m exceeds 1.03, like as specimen No. 54, the sintering properties becomes considerably lowered. Thus, the molar ratio of the barium site to titanium site has been limited to a value ranging from 1.000 to 1.03.

The reasons why the added amount of additives MnO , Fe_2O_3 , Cr_2O_3 , CoO and NiO , has been limited to the above range are as follows: If the added amount of the additive is less than 0.02 mole per 100 mole of the main component, like as specimen No. 34, the insulation resistance at $85^\circ C$ and above becomes small, resulting in lowering of the reliability in a long use at high temperatures. If the added amount of the additive exceeds 2.0 moles per 100 mole of the main component, like as specimen No. 53, the dielectric loss exceeds 1.5% and the insulation resistance becomes lowered.

EXAMPLE 4

Using the calcined powders of specimen Nos. 29, 30, 36 and 44 prepared in Example 3 and having particle size of not more than $1\ \mu m$, there were prepared monolithic ceramic capacitors in the same manner as Example 2.

Separate from the above, using, as raw materials, $BaCO_3$, $SrCO_3$, $CaCO_3$, TiO_2 , ZrO_2 , HfO_2 , MgO , MnO and NiO with the purity of not less than 99.8%, there was prepared a calcined powder for comparative specimen No. 55 in the following manner: The raw materials were weighed and mixed



so that the resultant product has a composition
99.5 mol $\{(\text{Ba}_{0.93}\text{Sr}_{0.05}\text{Ca}_{0.02})\text{O}\}_{1.01}(\text{Ti}_{0.83}\text{Zr}_{0.16}\text{Hf}_{0.01})\text{O}_2 + 0.5$
mol MgO + 0.3 mol MnO + 0.1 mol NiO. The resultant mixture
of the raw materials was wet-milled with a ball mill for 16
hours, dried by evaporation, calcined in air at 1100 °C for
2 hours, and then crushed and pulverized by a dry grinding
machine to prepare a calcined powder with a particle size of
1 μm or below.

Using the calcined powders, there were prepared
specimens (No. 55) of monolithic ceramic capacitors in the
same manner as Example 2.

The monolithic ceramic capacitors have the
following dimensions and constituents:

Width: 1.6 mm

Length: 3.2 mm

Thickness: 1.2 mm

Thickness of each dielectric layer: 15 μm

Number of effective dielectric layers: 19 sheets

Surface area of internal electrode: 2.1 mm²

For each specimen, electrical properties were measured
in the same manner as Example 2. Results are shown in Table
7.

Table 7

No.	Firing temp. (°C)	ϵ	$\tan \delta$ (%)	$\Delta C/C_{20^\circ\text{C}}(\%)$		CR ($\text{M}\Omega \cdot \mu\text{F}$)		mean life time(h)	$\Delta C'/C_0$ (%)	grain size (μm)
				-25°C	85°C	25°C	85°C			
*29	1270	15100	4.0	-57	-75	19,800	12,500	40	-6	3.9
*30	1270	8800	7.8	-52	-64	23,300	17,700	146	-19	2.0
36	1270	16800	3.5	-51	-77	30,400	16,900	196	-4	2.3
44	1270	17900	4.3	-48	-80	33,600	19,200	155	-6	3.0
*55	1270	14900	4.1	-43	-79	21,100	13,500	5	-22	4.1

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As can be seen from the results shown in Table 7, the monolithic ceramic capacitors including the non-reducible dielectric ceramic composition of the present invention are high in dielectric constant, small in dielectric loss ($\tan \delta$) and possess good temperature characteristics as the temperature coefficient of capacitance ($\Delta C/C_{20}$) meets requirements of F characteristics defined by JIS in the temperature range of -25°C to $+85^{\circ}\text{C}$. In addition, the composition of the present invention has an high insulation resistance as the product of C and R is more than $10000 \text{ M}\Omega \cdot \mu\text{F}$ at 25°C and more than $5000 \text{ M}\Omega \cdot \mu\text{F}$ at 85°C . Further, the composition has a long high temperature life time of more than 100 hours and the change rate of capacitance under the high temperature load test is less than 10 %.

In contrast therewith, the specimen No. 29 containing no element R1 selected from the group consisting of La, Ce, Nd is short in high temperature life time. The specimen No. 30 containing no element R2 selected from the group consisting of Dy, Ho, Er, Yb and Y is low in dielectric constant, but large in dielectric loss. In addition, the change rate of capacitance become large when the capacitor is subjected to the high temperature load test for 1000 hours.

The specimen No. 55, which does not contain R1 and R2, is short in high temperature life time, but large in

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change rate of capacitance. Thus, it can be seen that the co-addition of R1 and R2 contributes to improve both the high temperature life time and aging characteristics.

Although in all the examples described above, the starting materials used are powders of oxides or carbonates such as BaCO_3 , SrCO_3 , TiO_2 , ZrO_2 and HfO_2 , they may be powders prepared by the alkoxide method, coprecipitation method, or hydrothermal synthesis. The use of such powders has a great potential for further improvement in the electrical characteristics, as compared with those used in the above examples.

Although the present invention has been particularly described, it is to be noted that the same is by way of example only and is not to be taken by way of limitation, and the spirit and scope of the present invention is determined only by the terms of the appended claims.

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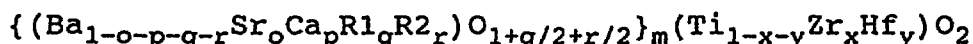


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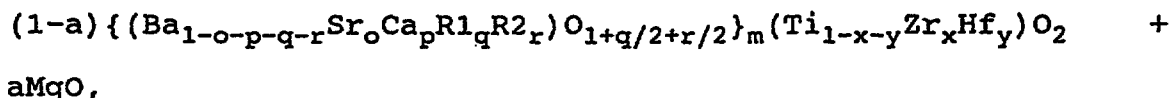
WHAT IS CLAIMED IS:

1. A non-reducible dielectric ceramic composition consisting essentially of a main component and at least one oxide selected from the group consisting of oxides of Mn, Fe, Cr, Co and Ni, said main component having a composition of the general formula (I):



wherein R1 is at least one element selected from the group consisting of La, Ce, Nd, Pr and Sm, R2 is at least one element selected from the group consisting of Dy, Ho, Er, Yb and Y, and wherein o, p, q, r, x, y and m meet the following conditions: $0 < o \leq 0.32$, $0 \leq p \leq 0.20$, $0 < q \leq 0.02$, $0 < r \leq 0.02$, $0 < x \leq 0.24$, $0 < y \leq 0.16$, $1.00 \leq m \leq 1.03$, and $0 < q+r \leq 0.03$; the content of said oxide being 0.02 to 2.0 moles per 100 moles of said main component when calculated in terms of respective oxides, MnO, Fe₂O₃, Cr₂O₃, CoO and NiO.

2. A non-reducible dielectric ceramic composition consisting essentially of a main component and at least one additive selected from the group consisting of oxides of Mn, Fe, Cr, Co and Ni, said main component having a composition of the general formula (II):



where R1 is at least one element selected from the group consisting of La, Ce, Nd, Pr and Sm, R2 is at least one

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element selected from the group consisting of Dy, Ho, Er, Yb and Y, and a, o, p, q, r, x, y and m meet the following conditions: $0 < a \leq 0.05$, $0 < o \leq 0.32$, $0 \leq p \leq 0.20$, $0 < q \leq 0.02$, $0 < r \leq 0.03$, $0 < x \leq 0.24$, $0 < y \leq 0.16$, $1.00 \leq m \leq 1.03$, and $0 < q+r \leq 0.04$; the content of said additive being 0.02 to 2.0 moles per 100 moles of said main component when calculated in terms of respective oxides, MnO, Fe₂O₃, Cr₂O₃, CoO and NiO.

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