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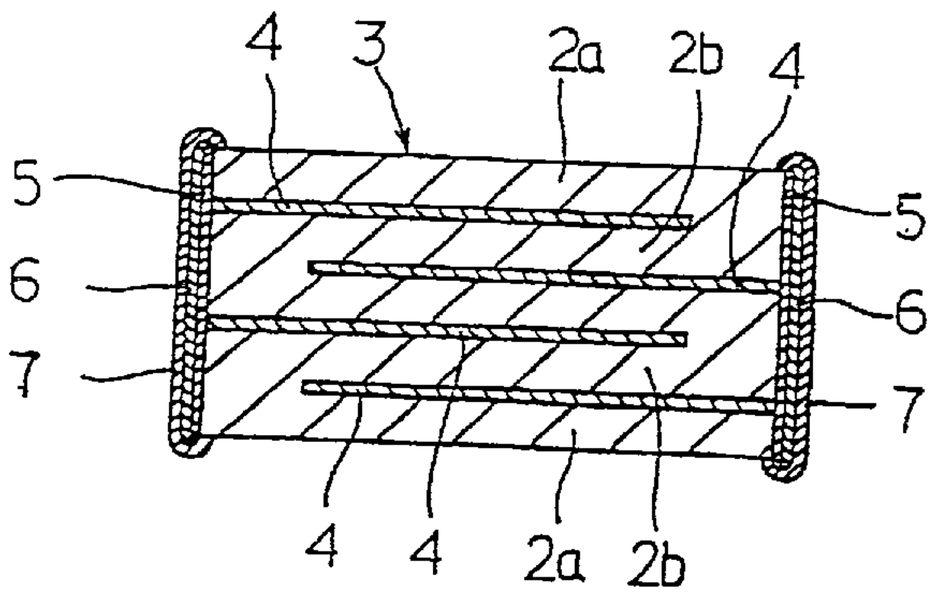
(54) **COMPOSITION D'UNE CERAMIQUE DIELECTRIQUE ET SON USAGE DANS UN CONDENSATEUR FORME D'UN BLOC DE CERAMIQUE**

(54) **DIELECTRIC CERAMIC COMPOSITION AND MONOLITHIC CERAMIC CAPACITOR USING SAME**



(57) On présente une composition de céramique diélectrique et un condensateur de céramique monolithique utilisant cette composition. La composition de céramique diélectrique comprend : du titanate de baryum; au moins un oxyde de terres rares tel que l'oxyde de terbium, l'oxyde de dysprosium, l'oxyde d'holmium, l'oxyde d'erbium et l'oxyde d'ytterbium; de l'oxyde de manganèse et de l'oxyde de nickel; et de l'oxyde de magnésium dont la quantité varie entre 0,5 et 3,0 mols en termes de MgO, et de l'oxyde de silicone en quantité variant entre 0,2 et 5,0 mols en termes de SiO_2, environ 100 mols de la composante essentielle dont la formule est la suivante : $(1-\alpha-\beta)\{BaO\}m \cdot TiO_2 + \alpha Re_2O_3 + \beta(Mn_{1-x}Ni_x)O$ où Re_2O_3 représente au moins une sélection de Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3 et Yb_2O_3; et α, β, m et x sont comme suit : $0,0025 < \alpha < 0,020$ $0,0025 < \beta < 0,04$ $\beta/\alpha < 4$ $0 < x < 1,0$ $1,000 < m < 1,035$.

(57) A dielectroc ceramic composition and a monolithic ceramic capacitor using the composition are provided. The dielectric ceramic composition includes: barium titanate; at least one rare earth oxide selected from terbium oxide, dysprosium oxide, holmium oxide, erbium oxide and ytterbium oxide; manganese oxide and nickel oxide; and magnesium oxide in an amount of from 0.5 to 3.0 mols in terms of MgO, and silicon oxide in an amount of from 0.2 to 5.0 mols in terms of SiO_2, relative to 100 mols of the essential component having the following compositional formula: $(1-\alpha-\beta)\{BaO\}m \cdot TiO_2 + \alpha Re_2O_3 + \beta (Mn_{1-x} Ni_x)O$ where Re_2O_3 is at least one selected from Tb_2O_3, Dy_2O_3 Ho_2O_3, Er_2O_3 and Yb_2O_3; and α, β , m and x are as follows: $0.0025 < \alpha < 0.020$ $0.0025 < \beta < 0.04$ $\beta/\alpha < 4$ $0 < x < 1.0$ $1.000 < m < 1.035$.

MURATA 5090260-5090266 June 20, I997

ABSTRACT

A dielectroc ceramic composition and a monolithic ceramic capacitor using the composition are provided. The dielectric ceramic composition includes: barium titanate; at least one rare earth oxide selected from terbium oxide, dysprosium oxide, holmium oxide, erbium oxide and ytterbium oxide; manganese oxide and nickel oxide; and magnesium oxide in an amount of from 0.5 to 3.0 mols in terms of MgO, and silicon oxide in an amount of from 0.2 to 5.0 mols in terms of SiO_2, relative to 100 mols of the essential component having the following compositional formula:

$$(1-\alpha-\beta)\{BaO\}_m \cdot TiO_2 + \alpha Re_2O_3 + \beta(Mn_{1-x}Ni_x)O$$

where Re_2O_3 is at least one selected from Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3 and Yb_2O_3; and

α, β, m and x are as follows:

$0.0025 \leq \alpha \leq 0.020$

$0.0025 \leq \beta \leq 0.04$

$\beta/\alpha \leq 4$

$0 \leq x < 1.0$

$1.000 < m \leq 1.035$.

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DIELECTRIC CERAMIC COMOSITION AND MONOLITHIC CERAMIC CAPACITOR USING SAME

FIELD OF THE INVENTION

The present invention relates to dielectric ceramic composition and monolithic ceramic capacitors using same to be used in electronic instruments, especially those having inner electrodes made of nickel or nickel alloys.

BACKGROUND OF THE INVENTION

Monolithic ceramic capacitors are generally produced as follows.

First, sheets of dielectric ceramic layers each as coated with an electrode material to be an inner electrode thereon are prepared. For example, the dielectric ceramic layers may consist essentially of $BaTiO_3$. Next, a plurality of such sheets of dielectric ceramic layers each coated with the electrode material are laminated and integrated under heat and pressure, and the resulting laminate is baked in a natural atmosphere at from 1250°C to 1350°C to obtain a monolithic dielectric ceramic body having inner electrodes therein. To the both ends of the dielectric ceramic body, are fixed and baked outer electrodes that electrically communicate with the inner electrode. Thus is obtained a monolithic ceramic capacitor.

Accordingly, the materials for such inner electrodes must satisfy the following requirements.

1. Since the ceramic laminate and the inner electrodes are baked together, the melting point of the materials for the inner electrodes must be not lower than the temperature at which the ceramic laminate can be baked.

2. The materials for the inner electrodes must not be oxidized even in high-temperature, oxidizing atmospheres and must not react with the dielectric ceramic layers.

As electrodes that satisfy these requirements, noble metals, such as platinum, gold, palladium and silver-palladium alloys, have heretofore been used.

However, these electrode materials are expensive, though having excellent characteristics. Accordingly, the cost of the electrode material reaches from 30 to 70 % of the total cost of one monolithic ceramic capacitor, which therefore is the essential factor of increasing the production costs of conventional monolithic ceramic capacitors.

Except for noble metals, known are base metals, such as Ni, Fe, Co, W and Mo, which have a high melting point. However, such base metals are easily oxidized in high-temperature, oxidizing atmospheres to lose their functions as electrodes. Therefore, if such base metals are used as the inner electrodes in monolithic ceramic capacitors, they

must be baked in neutral or reducing atmospheres along with dielectric ceramic layers. However, conventional dielectric ceramic materials were defective in that, if they are baked in such neutral or reducing atmospheres, they are greatly reduced into semiconductors.

In order to overcome these drawbacks, for example, proposed were a dielectric ceramic material comprising a solid solution of barium titanate where the ratio of barium sites/titanium sites is over the stoichiometric ratio thereof, such as that disclosed in Japanese Patent Publication No. 57-42588; and a dielectric ceramic material comprising a solid solution of barium titanate and containing oxides of rare earth metals, such as La, Nd, Sm, Dy and Y, added thereto, such as that disclosed in Japanese Patent Application Laid-Open No. 61-101459.

Also proposed were a dielectric ceramic material having a composition of $BaTiO_3$-$CaZrO_3$-MnO-MgO, such as that disclosed in Japanese Patent Application Laid-Open No. 62-256422; and a dielectric ceramic material having a composition of $BaTiO_3$-(Mg,Zn,Sr,Ca)O-B_2O_3-SiO_2, such as that disclosed in Japanese Patent Publication No. 61-14611.

Using these dielectric ceramic materials, ceramic laminates were obtained, which are not converted into semiconductors even when baked in reducing atmospheres. As a result, it has become possible to produce monolithic

ceramic capacitors comprising inner electrodes of base metals such as nickel.

With the recent development in electronics, small-sized electronic parts have become required greatly in the art, and small-sized, large-capacity, monolithic ceramic capacitors are therefore required greatly therein.

For these reasons, the recent tendency in the art is rapidly toward dielectric ceramic materials having a higher dielectric constant and toward thinner dielectric ceramic layers. Accordingly, there is now a great demand for dielectric ceramic materials with high reliability having a high dielectric constant, in which the temperature-dependent variation is little.

However, the dielectric ceramic materials disclosed in Japanese Patent Publication No. 57-42588 and Japanese Patent Application Laid-Open No. 61-101459 were defective in that the crystals constituting the ceramic laminates made from the materials are large, though the ceramic laminates themselves may have a high dielectric constant, with the result that, if thin dielectric ceramic layers having a thickness of, for example, 10 μm or less are incorporated into monolithic ceramic capacitors, the number of ceramic crystals to be in one layer is reduced and therefore the reliability of the monolithic ceramic capacitors is lowered. In addition, the dielectric ceramic

materials were further defective in that the temperature-dependent variation in the dielectric constant of the dielectric ceramics is great. For these reasons, the conventional dielectric ceramic materials could not meet the requirements in the market.

On the other hand, the dielectric ceramic material disclosed in Japanese Patent Application Laid-Open No. 62-256422 was defective in that $CaZrO_3$ and also $CaTiO_3$ that is formed during the baking step may often form secondary phases together with Mn and others and therefore the high-temperature reliability of the capacitor comprising the material is problematic, although the dielectric constant of the ceramic body of the material is relatively high, the crystals constituting the ceramic laminate are small, and the temperature-dependent variation in the dielectric constant is small.

The dielectric ceramic material disclosed in Japanese Patent Publication No. 61-14611 was defective in that the dielectric constant of the ceramic body of the material is from 2000 to 2800 and therefore the material is not suitable for small-sized, large-capacity monolithic ceramic capacitors. In addition, the material was further defective in that it does not satisfy the X7R-level characteristic standard as stipulated in the EIA Standard, which indicates that the temperature-dependent variation in

the capacitance within the range between -55°C and +125°C shall be +/- 15 % or less.

Japanese Patent Publication No. 63-10386 discloses a non-reducing dielectric ceramic material, which, however, was defective in that its insulating resistance and the temperature-dependent variation in its capacity are greatly influenced by the grain size of the crystals of $BaTiO_3$ which is the essential component constituting the material and therefore the material is difficult to control so as to obtain stable characteristics. In addition, for the insulating resistance of the material, the product of the insulating resistance value and the capacitance value (product of CR) falls between 1000 and 2000 ($\Omega \cdot F$). In view of this, the material could not be practicable.

Although some improvements were made in the non-reducing dielectric ceramic compositions that have heretofore been proposed in the art, such as those mentioned hereinabove, to make them have good insulation resistance in high-temperature load life tests, the improvement in their insulation resistance in moisture-resistant load tests was still unsatisfactory as yet.

In order to solve the above-mentioned problems, proposed were different compositions, for example, in Japanese Patent Application Laid-Open Nos. 05-09066, 05-09067 and 05-09068. However, these compositions could not

still satisfy the recent severe requirements for small-sized, large-capacity capacitors in the market. Specifically, the recent requirements for these in the market are to make them have much thinner dielectric ceramic layers and even have high reliability. Therefore, there is still a great demand for dielectric ceramic materials capable of producing much thinner dielectric ceramic layers in monolithic ceramic capacitors with much higher reliability. Given the situation, accordingly, it has become necessary to provide small-sized, large-capacity, high-reliability monolithic ceramic capacitors still having highly-reliable characteristics even in high-temperature and high-humidity conditions.

SUMMARY OF THE INVENTION

Accordingly, the subject matter of the present invention is to provide a low-priced, small-sized, large-capacity, monolithic ceramic capacitor, which has a dielectric constant of 3000 or more, which has a high insulation resistance, when measured at room temperature and 125°C, of 6000 MΩ·μF or more and 2000 MΩ·μF or more, respectively, in terms of its product with the capacitance (the product of CR), which has temperature-dependent capacitance that satisfies the B-level characteristic standard as stipulated in the JIS Standard and the X7R-

level characteristic standard as stipulated in the EIA Standard, and which has good weather resistance even in high-temperature and high-humidity load conditions.

The present invention has been made in consideration of the above-mentioned object.

Specifically, the present invention provides a monolithic ceramic capacitor composed of; a plurality of dielectric ceramic layers, a plurality of inner electrodes as formed between the dielectric ceramic layers in such a manner that one end of each inner electrode is exposed out of either end of the dielectric ceramic layers, and outer electrodes as electrically connected with the exposed inner electrodes, which is characterized in that;

the dielectric ceramic layers each are made of a material comprising; barium titanate having a content of impurities, alkali metal oxides of 0.02 % by weight or less; at least one rare earth oxide selected from terbium oxide, dysprosium oxide, holmium oxide, erbium oxide and ytterbium oxide; and manganese oxide and nickel oxide; and containing side components, magnesium oxide in an amount of from 0.5 to 3.0 mols in terms of MgO, and silicon oxide in an amount of from 0.2 to 5.0 mols in terms of SiO_2, relative to 100 mols of the essential component having the following compositional formula:

$$(1-\alpha-\beta)\{BaO\}_m \cdot TiO_2 + \alpha Re_2O_3 + \beta(Mn_{1-x}Ni_x)O$$

where Re_2O_3 is at least one selected from Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3 and Yb_2O_3; and

α, β, m and x are as follows:

$0.0025 \leq \alpha \leq 0.020$

$0.0025 \leq \beta \leq 0.04$

$\beta/\alpha \leq 4$

$0 \leq x < 1.0$

$1.000 < m \leq 1.035$; and

the inner electrodes each are made of nickel or a nickel alloy.

Preferably, in the monolithic ceramic capacitor of the present invention, the outer electrodes each are made of a sintered layer of an electroconductive metal powder or of an electroconductive metal powder with glass frit added thereto. Further preferably, the outer electrodes each are composed of a first, sintered layer of an electroconductive metal powder or of an electroconductive metal powder with glass frit added thereto, and a second, plated layer formed on the first layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view illustrating the outline of one embodiment of the monolithic ceramic capacitor of the present invention.

Fig. 2 is a plan view illustrating the outline of one embodiment of a dielectric ceramic layer having an inner electrode thereon, which is prepared in the present invention.

Fig. 3 is a perspective, exploded view illustrating one embodiment of a ceramic laminate as prepared in the present invention.

PREFERRED MODES OF CARRYING OUT THE INVENTION

Now, preferred modes of carrying out the invention are described in detail hereinunder.

As the material for the dielectric ceramic layers constituting the monolithic ceramic capacitor of the present invention, herein used is a dielectric ceramic material comprising barium titanate, terbium oxide, dysprosium oxide, holmium oxide, erbium oxide, ytterbium oxide, manganese oxide and nickel oxide, in a specifically conditioned compositional ratio such as that mentioned hereinabove, and containing magnesium oxide and silicon oxide within the range as defined hereinabove. Therefore, even in a reducing atmosphere, the dielectric ceramic material can be baked well without worsening its characteristics. As a result, according to the present invention, it is possible to obtain a high-reliability, monolithic ceramic capacitor having a temperature-dependent

capacitance that satisfies the B-level characteristic standard as stipulated in the JIS Standard and also the X7R-level characteristic standard as stipulated in the EIA Standard, and having high insulation resistance at room temperature and even at high temperatures.

It has been confirmed that, of the essential components constituting the dielectric ceramic material for use in the present invention, such as barium titanate, terbium oxide, dysprosium oxide, holmium oxide, erbium oxide, ytterbium oxide, manganese oxide and nickel oxide, the content of the impurities in the barium titanate, such as alkaline earth metal oxides, e.g., SrO and CaO; alkali metal oxides, e.g., Na_2O and K_2O; and other oxides, e.g., Al_2O_3 and SiO_2, especially that of alkali metal oxides such as Na_2O and K_2O, has a great influence on the electric characteristics of the capacitor of the invention. Specifically, it has been confirmed that, if barium titanate having an alkali metal oxide impurity content of smaller than 0.02 % by weight is in the dielectric ceramic material, the capacitor of the invention comprising the dielectric ceramic may have a dielectric constant of 3000 or higher.

The reason why silicon oxide is added to the dielectric ceramic layers in the present invention is that said addition improves the sinterability of the layers if

the sintering atmosphere is controlled to have an oxygen partial pressure near to the equilibrated oxygen partial pressure of Ni/NiO at relatively high temperatures during the sintering step, while also improving the moisture-resistant load characteristics of the capacitors comprising the layers.

If the dielectric ceramic material mentioned hereinabove is used to form the dielectric ceramic layers constituting the monolithic ceramic capacitor of the invention, it is possible to use base metals, nickel or nickel alloys to form the inner electrodes of the capacitor. In addition, it is also possible to add a small amount of ceramic powder to the inner electrodes along with nickel or nickel alloys.

The composition of the outer electrodes of the capacitor of the invention is not specifically defined. Concretely, for example, the outer electrodes may be made of sintered layers of various electroconductive metal powders, such as Ag, Pd, Ag-Pd, Cu or Cu alloys, or sintered layers comprising such electroconductive metal powders and various types of glass frit of B_2O_3-Li_2O-SiO_2-BaO, B_2O_3-SiO_2-BaO, Li_2O-SiO_2-BaO, B_2O_3-SiO_2-ZnO or the like. If desired, a small amount of ceramic powder may be added to the sintered layers comprising such electroconductive metal powders and optionally glass frit.

More preferably, the sintered layers are coated with a plate layer. The plate layer may comprise Ni, Cu, Ni-Cu alloys or the like, and may be further coated with any additional plate layer of solder, tin or the like.

Now, the present invention is described in more detail with reference to the following Examples, which, however, are not intended to restrict the scope of the invention.

One embodiment of the monolithic ceramic capacitor of the present invention is referred to. Fig. 1 is a cross-sectional view illustrating the outline of one embodiment of the monolithic ceramic capacitor of the invention. Fig. 2 is a plan view illustrating the outline of the dielectric ceramic layer having an inner electrode thereon, which is in this embodiment. Fig. 3 is a perspective, exploded view illustrating the ceramic laminate to be in this embodiment.

As in Fig. 1, the monolithic ceramic capacitor 1 of the present invention is in the form of a rectangular parallelepiped chip, in which the outer electrodes 5, the first plate layers 6 made of nickel, copper or the like, and the second plate layers 7 made of solder, tin or the like are formed on the both sides of the ceramic laminate 3 as formed through lamination of a plurality of dielectric ceramic layers 2a and 2b via the inner electrode 4 therebetween.

Now, a method for producing the monolithic ceramic capacitor 1 of the invention is described below in the order of the steps constituting the method.

First, the ceramic laminate 3 is formed. This ceramic laminate 3 is produced as follows. As in Fig. 2, a raw material powder comprising barium titanate; at least one or more rare earth oxides selected from terbium oxide, dysprosium oxide, holmium oxide, erbium oxide and ytterbium oxide; manganese oxide, nickel oxide, magnesium oxide; and oxides consisting essentially of silicon oxide is formed into a slurry, and then sheeted to prepare a dielectric ceramic layer 2a (green sheet). On one surface of the green sheet, formed is an internal electrode 4 of nickel or a nickel alloy. To form the internal electrode 4, employable is any method of screen printing, metal vapor deposition or plating.

A predetermined number of the dielectric ceramic layers 2b each with the inner electrode 4 formed thereon are laminated, and then sandwiched between two dielectric ceramic layers 2a with no inner electrode, as in Fig. 3, and these are integrated under pressure to give a laminate. Next, the resulting laminate composed of the dielectric ceramic layers 2a, 2b, . . . 2b, 2a is baked in a reducing atmosphere at a predetermined temperature to obtain the ceramic laminate 3.

Next, on the both sides of the ceramic laminate 3, formed are two outer electrodes 5 that are connected with the inner electrodes 4. The material of the outer electrodes 5 may be the same as that of the inner electrodes 4. Apart from this, silver, palladium, silver-palladium alloys, copper, copper alloys and others can be used as the material of the outer electrodes 5, to which can be added glass frit, such as glass of the type of B_2O_3-SiO_2-BaO or Li_2O-SiO_2-BaO. In consideration of the use of the monolithic ceramic capacitor of the invention and the site at which the capacitor is used, suitable materials are selected for the outer electrodes 5. The outer electrodes 5 can be formed by applying a paste material of metal powder onto the baked ceramic laminate 3 followed by baking it. Alternatively, the paste material can be applied onto the non-baked ceramic laminate 3, which is baked all at a time. After this, the outer electrodes 5 may be plated with nickel, copper or the like to form a first plate layer 6 thereon. Last, the first plate layer 6 is coated with a second plate layer 7 of solder, tin or the like. Thus is produced the chip-type, monolithic ceramic capacitor 1 of the invention.

The following Example is to further illustrate the invention in more detail.

EXAMPLE 1

First, raw materials of $TiCl_4$ and $Ba(NO_3)_2$ having various degrees of purity were prepared and weighed. These were treated with oxalic acid to obtain a precipitate of barium titanyl oxalate ($BaTiO(C_2O_4)\cdot 4H_2O$). This precipitate was decomposed under heat at 1000°C or higher to obtain four types of barium titanate ($BaTiO_3$) as shown in Table 1.

Next, prepared were Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Yb_2O_3, MnO, NiO and MgO each having a purity of 99 % or more, and a colloidal silica containing silicon dioxide in an amount of 20 % by weight in terms of SiO_2.

[Table 1]

Type of $BaTiO_3$	Content of Impurities (wt.%)					Mean Grain Size (μm)
	Alkali Metal Oxides	SrO	CaO	SiO_2	Al_2O_3	
A	0.003	0.012	0.001	0.010	0.005	0.60
B	0.020	0.010	0.003	0.019	0.008	0.56
C	0.012	0.179	0.018	0.155	0.071	0.72
D	0.062	0.014	0.001	0.019	0.004	0.58

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Next, these raw materials were mixed in various compositional ratios as shown in Table 2 and Table 3 to prepare various compositions. Each composition was wet-milled in a ball mill, evaporated to dryness and dressed to obtain a powdery raw material mixture.

The resulting mixture was wet-milled in a ball mill along with a polyvinyl butyral binder and an organic solvent such as ethanol to obtain a ceramic slurry. This ceramic slurry was sheeted according to doctor blading to obtain a rectangular green sheet having a thickness of 11 μm. Next, an electroconductive paste consisting essentially of Ni was printed on this ceramic green sheet to form thereon an electroconductive paste layer, which is formed into an inner electrode.

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[Table 2]

Sample No.	$(1-\alpha-\beta)\{BaO\}m\cdot TiO_2 + \alpha Re_2O_3 + \beta(Mn_{1-x}Ni_x)O$											MgO (mol)	SiO_2 (mol)
	Type of $BaTiO_3$	α						β	x	β/α	m		
		Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Yb_2O_3	Total						
*1	A	-	-	-	-	-	0.0000	0.005	0.3	-	1.010	1.20	1.00
*2	A		0.008		0.002		0.0100	0.000	-	0	1.010	1.20	1.00
*3	A		0.008		0.002		0.0100	0.005	0.3	1/2	0.990	1.20	1.00
*4	A			0.0100			0.0100	0.005	0.3	1/2	1.000	1.00	1.00
*5	A		0.0020	0.0080			0.0100	0.0100	0.3	1	1.010	0.00	1.00
*6	A		0.008				0.0080	0.0080	0.3	1	1.015	1.20	0.00
*7	A			0.0075			0.0075	0.0075	0.5	1	1.015	1.50	0.10
8	A	0.0015	0.0010				0.0025	0.0025	0.1	1	1.005	0.50	0.20
9	A		0.0075			0.0025	0.0100	0.0080	0.5	4/5	1.010	1.00	1.00
10	A		0.0060			0.0060	0.0120	0.0080	0.0	2/3	1.010	1.50	1.50
11	A	0.0030			0.0060		0.0090	0.0090	0.4	1	1.015	1.20	1.50
12	A	0.0040		0.0040			0.0080	0.0080	0.3	1	1.010	1.20	1.00
13	C		0.010		0.0100		0.0200	0.0400	0.8	2	1.005	1.00	2.00
14	B	0.0030					0.0030	0.0060	0.4	2	1.010	3.00	5.00
15	A				0.008	0.002	0.0100	0.0050	0.0	1/2	1.010	1.00	1.50
16	A			0.0060			0.0060	0.0240	0.6	4	1.035	0.50	2.50
17	A		0.0080			0.012	0.0200	0.0050	0.1	1/4	1.015	2.00	1.50

[Table 3]

Sample No.	$(1-\alpha-\beta)\{BaO\}m \cdot TiO_2 + \alpha Re_2O_3 + \beta(Mn_{1-x}Ni_x)O$											MgO (mol)	SiO_2 (mol)
	Type of $BaTiO_3$	α						β	x	β/α	m		
		Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Yb_2O_3	Total						
*18	A			0.020		0.010	0.030	0.015	0.3	1/2	1.010	2.00	1.50
*19	A		0.010		0.005		0.015	0.060	0.3	4.0	1.010	1.20	1.50
*20	A		0.010				0.010	0.010	1.0	1.0	1.010	1.20	1.00
*21	A	0.0050					0.0050	0.040	0.3	8.0	1.010	1.20	1.00
*22	A		0.010				0.010	0.0050	0.3	1/2	1.050	1.20	2.00
*23	A		0.010				0.010	0.0050	0.3	1/2	1.010	5.0	2.00
*24	A		0.010				0.010	0.0050	0.3	1/2	1.010	1.20	8.00
*25	D		0.010				0.010	0.0050	0.3	1/2	1.010	1.20	1.50

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A plurality of these ceramic green sheets each having the electroconductive paste layer formed thereon were laminated in such a manner that the side of one sheet with the electroconductive paste exposed out of it was alternated with that of another sheet with the electroconductive paste not exposed out of it. Thus was obtained a laminate. This laminate was heated in an N_2 atmosphere at 350°C whereby the binder was burnt out, and then baked for 2 hours in a reducing atmosphere comprising gases of H_2, N_2 and H_2O and having an oxygen partial pressure of from 10^{-11} to 10^{-8} MPa, at various temperatures shown in Table 4, to obtain sintered ceramic bodies.

The surface of each sintered ceramic body was observed with a scanning, electronic microscope at a magnification of 1500 times, to determine the grain sizes of the grains seen in the field of view.

A silver paste containing glass frit of the type of B_2O_3-Li_2O-SiO_2-BaO was applied onto the both sides of each sintered ceramic body, and baked again in an N_2 atmosphere at 600°C to thereby form outer electrodes as electrically connected with the inner electrodes.

The outer dimension of each of these monolithic capacitors thus obtained was 1.6 mm width x 3.2 mm length x 1.2 mm thickness, and the thickness of each dielectric

ceramic layer as sandwiched between the inner electrodes was 8 μm.

The total number of the effective dielectric ceramic layers was 19, and the area of the facing electrodes per one ceramic layer was 2.1 mm^2.

The capacitance (C) and the dielectric loss (tan δ) of each sample were measured, using an automatic bridge-type meter at a frequency of 1 KHz, at 1 V rms and at 25°C. From the capacitance thus measured, obtained was the dielectric constant (ε) through calculation. Next, to measure the insulation resistance (R) of each sample, a direct current voltage of 16 V was applied to each sample at 25°C or 125°C for 2 minutes, using an insulation resistance meter. After having thus measured the insulation resistance (R) of each sample, the product of the capacitance (C) and the insulation resistance (R) or, that is, the product of CR of each sample was obtained. In addition, the temperature-dependent variation in the capacitance of each sample was determined.

For the temperature-dependent variation in the capacitance, obtained were the variation in the capacitance between -25°C and 85°C based on the capacitance at 20°C ($\Delta C/C_{20°C}$), the variation in the capacitance between -55°C and 125°C based on the capacitance at 25°C ($\Delta C/C_{25°C}$), and

the maximum variation, in terms of the absolute value, between -55°C and 125°C ($|\Delta C|max$).

To determine the high-temperature load life of each sample, 36 pieces of each sample were subjected to a high-temperature load test, in which a direct current voltage of 100 V was applied to each piece at 150°C, while measuring the insulation resistance of each test piece which varied time-dependently. In this test, the period of time within which the insulation resistance value (R) of each piece being tested reached 10^6 Ω or lower was measured, which is referred to as the life time of each test piece. The average of all the tested pieces was calculated to obtain the average life time of each sample.

In addition, to measure the moisture-resistant load life of each sample, 72 pieces of each sample were subjected to a high-humidity load test, in which a direct current voltage of 16 V was applied to each piece at 121°C under 2 atmospheres (relative humidity: 100 %), while measuring the insulation resistance of each test piece which varied time-dependently. In this test, the number of the test pieces that had an insulation resistance value (R) of 10^6 Ω or lower within a period of 250 hours was counted. The results obtained in these tests are shown in Table 4.

[Table 4]

Sample No.	Baking Temp. (°C)	Dielectric Constant, ε	Dielectric Loss, tan δ (%)	Temperature-Dependent Variation in Capacitance, ΔC/C20°C (%)		Temperature-Dependent Variation in Capacitance, ΔC/C25°C (%)			Product of CR (Ω•F), at 25°C	Product of CR (Ω•F), at 125°C	Mean Life Time (hr.)	Number of Test Pieces Failed in Moisture-Resistant Load Test	Grain Size (μm)
				-25°C	85°C	-55°C	125°C	max	16V	16V			
*1	1300	3090	2.3	-12.1	-4.5	-16.3	2.2	16.3	8200	1880	7	0/72	0.77
*2	1280	As semiconductors were formed, the measurement was impossible.											2.4
*3	1280	As semiconductors were formed, the measurement was impossible.											2.1
*4	1280	3420	2.3	-3.3	-6.2	-3.4	-6.5	6.5	2360	570	158	0/72	0.75
*5	1280	3390	2.0	0.1	-10.5	0.7	-16.3	16.3	4700	1510	302	0/72	0.74
*6	1360	As the sample was sintered insufficiently, the measurement was impossible.											0.61
*7	1330	3250	2.0	-3.2	-5.5	-3.2	-5.9	5.9	4400	1820	310	51/72	0.68
8	1300	4110	2.5	-7.1	-7.4	-11.9	-13.8	13.8	7700	4630	325	0/72	0.72
9	1280	3320	1.9	-2.4	-5.5	-2.5	-6.7	6.7	5980	2320	503	0/72	0.68
10	1300	3120	1.8	-3.0	-4.3	-3.2	-4.7	4.8	6100	2230	548	0/72	0.69
11	1280	3490	2.0	-1.2	-7.2	-0.3	-10.2	105	6550	2480	526	0/72	0.71
12	1280	3570	2.1	-1.5	-7.6	-1.0	-9.4	11.8	6660	2850	518	0/72	0.72
13	1300	3050	1.5	-1.9	-4.8	-1.8	-5.4	5.5	6060	2040	601	0/72	0.78
14	1260	3430	1.9	-3.7	-7.0	-4.4	-10.9	11.0	7380	3970	356	0/72	0.64
15	1280	3330	2.0	-0.8	-6.1	-1.4	-6.2	6.2	6090	2120	388	0/72	0.69
16	1300	3380	1.8	-0.4	-9.0	-2.0	-12.3	12.3	6870	2450	311	0/72	0.68
17	1300	3010	1.5	-1.6	-3.5	-2.2	-2.7	3.8	6060	2040	632	0/72	0.68
*18	1360	2310	1.3	-2.2	-2.3	-3.5	-2.4	3.6	3840	1010	213	7/72	0.65
*19	1280	3070	1.8	-0.2	-9.6	-0.2	-15.9	15.9	5630	510	112	0/72	0.70

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As is obvious from Table 1, Table 2, Table 3 and Table 4, the monolithic ceramic capacitor samples falling within the scope of the present invention all were found to have a high dielectric constant ε of not lower than 3,000, and have a dielectric loss tangent, tan δ, of not larger than 2.5 %, while satisfying the B-level characteristic standard as stipulated in the JIS Standard within the temperature range between -25°C and 85°C and also the X7R-level characteristic standard as stipulated in the EIA Standard within the temperature range between -55°C and 125°C with respect to the temperature-dependent variation in the capacitance.

Moreover, these samples of the invention were found to have high insulation resistance values, when measured at 25°C and 125°C, of not smaller than 6,000 $M\Omega \cdot \mu F$ and not smaller than 2,000 $M\Omega \cdot \mu F$, respectively, in terms of the product of CR. Further, these were found to have a long mean life time of not shorter than 300 hours, and none of these failed in the moisture-resistant load test. In addition, these were sintered at relatively low temperatures of not higher than 1300°C, and the crystal grains in the sintered samples were small to have grain sizes of not larger than 1 μm. Since the crystal grains existing in the dielectric ceramic layers in these samples are small, or that is, not larger than 1 μm, the number of

the crystal grains to be in one dielectric ceramic layer is large. Accordingly, even if the ceramic laminate comprising these layers is thinned, the reliability of the capacitor comprising the laminate is not lowered.

Now, the reasons for defining the compositions for use in the present invention are mentioned below.

First referred to are the reasons for defining α to fall within the range of $0.0025 \leq \alpha \leq 0.020$ in the composition of $(1-\alpha-\beta)\{BaO\}_m \cdot TiO_2 + \alpha Re_2O_3 + \beta(Mn_{1-x}Ni_x)O$, in which Re_2O_3 is at least one selected from Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3 and Yb_2O_3. As in Sample No. 1, if the amount, α, of Re_2O_3 is smaller than 0.0025, the temperature-dependent variation in the capacitance is great, the insulation resistance at 125°C is low, and the mean life time is very short.

On the other hand, as in Sample No. 18, if the amount, α, of Re_2O_3 is larger than 0.020, the dielectric constant is not larger than 3,000, the insulation resistance at 25°C and 125°C is low, the mean life time is short, some test pieces failed in the moisture-resistant load test, and the sintering temperature is high.

The reasons for defining β to fall within the range of $0.0025 \leq \beta \leq 0.04$ are as follows. As in Sample No. 2, if the amount, β, of (Mn,Ni)O is smaller than 0.0025, the dielectric ceramics were reduced into semiconductors, when

baked in the reducing atmosphere, to thereby lower the insulation resistance.

As in Sample No. 19, if the amount, β, of (Mn,Ni)O is larger than 0.04, the insulation resistance at 25°C and at 125°C is lower than 6,000 $M\Omega \cdot \mu F$ and 2,000 $M\Omega \cdot \mu F$, respectively, the mean life time is shorter than 300 hours, and the temperature-dependent variation in the capacitance is too large to satisfy the X7R-level characteristic standard of the EIA Standard.

The reasons for defining β/α to fall within the range of $\beta/\alpha \leq 4$ are as follows. As in Sample No. 21, if the ratio, β/α, of the amount β of (Mn,Ni)O to the amount α of Re_2O_3 is larger than 4, the temperature-dependent variation in the capacitance is large, the insulation resistance at 125°C is lower than 2000 $M\Omega \cdot \mu F$, and the mean life time is shorter than 300 hours.

The reasons for defining x to fall within the range of $0 \leq x < 1.0$ are as follows. As in Sample No. 20, if the amount of NiO, x, is 1.0, the insulation resistance at 25°C and at 125°C is lower than 6,000 $M\Omega \cdot \mu F$ and 2,000 $M\Omega \cdot \mu F$, respectively, and the mean life time is shorter than 300 hours.

The reasons for defining m to fall within the range of $1.000 < m \leq 1.035$ are as follows. As in Sample Nos. 3 and 4, if the molar ratio, m, of barium titanate is not larger

than 1.000, the dielectric ceramic was converted into semiconductors when baked in the reducing atmosphere, whereby the insulation resistance of the capacitor was lowered (Sample No. 3); or the insulation resistance of the capacitor was lowered and the mean life time thereof was short so that the dielectric ceramic could not be used in preparing thin ceramic laminates (Sample No. 4).

On the other hand, as in Sample No. 22, if the molar ratio, m, is larger than 1.035, the sinterability of the sample is very poor.

The reasons for defining the magnesium oxide content to fall between 0.5 mols and 3.0 mols in terms of MgO are as follows. As in Sample No. 5, if the amount of MgO is smaller than 0.5 mols, the insulation resistance is low, and the temperature-dependent variation in the capacitance could not satisfy the X7R-level characteristic standard of the EIA standard though satisfying the B-level characteristic standard of the JIS Standard.

On the other hand, as in Sample No. 23, if the amount of MgO is larger than 3.0 mols, the sintering temperature shall be too high, the dielectric constant could not be over 3,000, and many test pieces of the sample failed in the moisture-resistant load test.

The reasons for defining the silicon oxide content to fall between 0.2 mols and 5.0 mols in terms of SiO_2 are as

follows. As in Sample No. 6, if the SiO_2 content is 0 (zero), the sample could not be sintered. As in Sample No. 7, if the SiO_2 content is smaller than 0.2 mols, the sintering temperature shall be too high, the insulation resistance is low, and many test pieces of the sample failed in the moisture-resistant load test.

On the other hand, as in Sample No. 24, if the SiO_2 content is larger than 5.0 mols, the dielectric constant could not be over 3000, and the insulation resistance at 125°C could not be over 2,000 $M\Omega \cdot \mu F$.

The reasons for defining the impurity, alkali metal oxide content of barium titanate to be not larger than 0.02 % by weight are as follows. As in Sample No. 25, if the impurity, alkali metal oxide content of barium titanate is larger than 0.02 % by weight, the dielectric constant is lowered.

In the above-mentioned Example, used was a powder of barium titanate as prepared according to the oxalic acid method, which, however, is not limitative. Apart from this, also employable are powders of barium titanate as prepared according to an alkoxide method or a hydrothermal reaction method. If the latter powders are used, the characteristics of the capacitors may often be improved more than those of the samples as demonstrated in the Example herein.

Powders of terbium oxide, dysprosium oxide, holmium oxide, erbium oxide, ytterbium oxide, manganese oxide, nickel oxide and others were used in the Example, which, however, are not also limitative. Solutions of alkoxides or organic metal compounds for such oxides can also be employed, in place of such oxide powders, without interfering with the characteristics of the capacitors produced, provided that they are formulated to constitute the dielectric ceramic layers falling within the scope of the present invention.

In the monolithic ceramic capacitor of the present invention, the dielectric ceramic layers are made from a dielectric ceramic material that can be baked even in a reducing atmosphere without being reduced into semiconductors. Therefore, a base metal of nickel or a nickel alloy can be used as the material for the electrodes in the capacitor. In addition, since the dielectric ceramic material can be baked at relatively low temperatures of 1300°C or lower, the production costs of the capacitor can be reduced.

Moreover, the monolithic ceramic capacitor of the invention that comprises ceramic layers made from such dielectric ceramic materials has a dielectric constant of 3000 or higher, and the temperature-dependent variation in the high dielectric constant of the capacitor is small.

Further, the capacitor has high insulation resistance and has good characteristics, and their characteristics are not worsened even in high-temperature and high-humidity conditions.

In addition, since the crystals constituting the dielectric layers are small to have grain sizes of 1 μm or smaller, the layers can be thinned well, without reducing the number of the crystals to be therein, being different from the ceramic layers constituting conventional monolithic ceramic capacitors. Therefore, according to the present invention, it is possible to obtain high-reliability, small-sized, large-capacity, monolithic ceramic capacitors.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

WHAT IS CLAIMED IS:

1. A dielectric ceramic composition comprising:

barium titanate;

at least one rare earth oxide selected from terbium oxide, dysprosium oxide, holmium oxide, erbium oxide and ytterbium oxide;

manganese oxide and nickel oxide; and

magnesium oxide, as a side component, in an amount of from 0.5 to 3.0 mols in terms of MgO, and silicon oxide in an amount of from 0.2 to 5.0 mols in terms of SiO_2, relative to 100 mols of the essential component having the following compositional formula:

$$(1-\alpha-\beta)\{BaO\}_m \cdot TiO_2 + \alpha Re_2O_3 + \beta(Mn_{1-x}Ni_x)O$$

where Re_2O_3 is at least one selected from Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3 and Yb_2O_3; and

α, β, m and x are as follows:

$0.0025 \leq \alpha \leq 0.020$

$0.0025 \leq \beta \leq 0.04$

$\beta/\alpha \leq 4$

$0 \leq x < 1.0$

$1.000 < m \leq 1.035$.

2. The dielectric ceramic composition according to claim 1, wherein said barium titanate having at least one alkali metal oxide as an impurity.

3. The dielectric ceramic composition according to claim 2, wherein said barium titanate includes alkali metal oxides of 0.02 % by weight or less.

4. The dielectric ceramic composition according to claim 2, wherein said alkali metal oxide includes at least one oxide selected from SrO, CaO, SiO_2 and Al_2O_3.

5. A monolithic ceramic capacitor comprising;

dielectric ceramic layers,

at least two inner electrodes as formed between the dielectric ceramic layers in such a manner that one end of each inner electrode is exposed out of either end of the dielectric ceramic layers, and

outer electrodes as electrically connected with the exposed inner electrodes,

wherein the dielectric ceramic layers each are made of a material comprising;

barium titanate;

at least one rare earth oxide selected from terbium oxide, dysprosium oxide, holmium oxide, erbium oxide and ytterbium oxide, and

manganese oxide and nickel oxide,

and containing side components, magnesium oxide in an amount of from 0.5 to 3.0 mols in terms of MgO, and silicon oxide in an amount of from 0.2 to 5.0 mols in terms of SiO_2, relative to 100 mols of the essential component having the following compositional formula:

$$(1-\alpha-\beta)\{BaO\}_m \cdot TiO_2 + \alpha Re_2O_3 + \beta(Mn_{1-x}Ni_x)O$$

where Re_2O_3 is at least one selected from Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3 and Yb_2O_3; and

α, β, m and x are as follows:

$0.0025 \leq \alpha \leq 0.020$

$0.0025 \leq \beta \leq 0.04$

$\beta/\alpha \leq 4$

$0 \leq x < 1.0$

$1.000 < m \leq 1.035$.

6. The monolithic ceramic capacitor according to claim 5, wherein said barium titanate having at least one alkali metal oxide as an impurity.

7. The monolithic ceramic capacitor according to claim 6, wherein said barium titanate includes alkali metal oxides of 0.02 % by weight or less.

8. The dielectric ceramic capacitor according to claim 6, wherein said alkali metal oxide includes at lest one oxide selected from SrO, CaO, SiO_2 and Al_2O_3.

9. The monolithic ceramic capacitor according to claim 5, wherein at least one of said inner electrodes is made of at least one base metal.

10. The monolithic ceramic capacitor according to claim 9, wherein said base metal electrode includes ceramic powder.

11. The monolithic ceramic capacitor according to claim 9, wherein said base metal is nickel or nickel alloy.

12. The monolithic ceramic capacitor according to claim 5, wherein at least one of said outer electrodes is made of a sintered layer of an electroconductive metal powder

13. The monolithic ceramic capacitor according to claim 5, wherein at least one of said outer electrodes is made of an electroconductive metal powder with glass frit added thereto.

14. The monolithic ceramic capacitor as claimed in claim 5, wherein the outer electrodes each comprising a first, sintered layer of an electroconductive metal powder or of an electroconductive metal powder with glass frit added thereto, and a second, plated layer formed on the first layer.

Fig 1

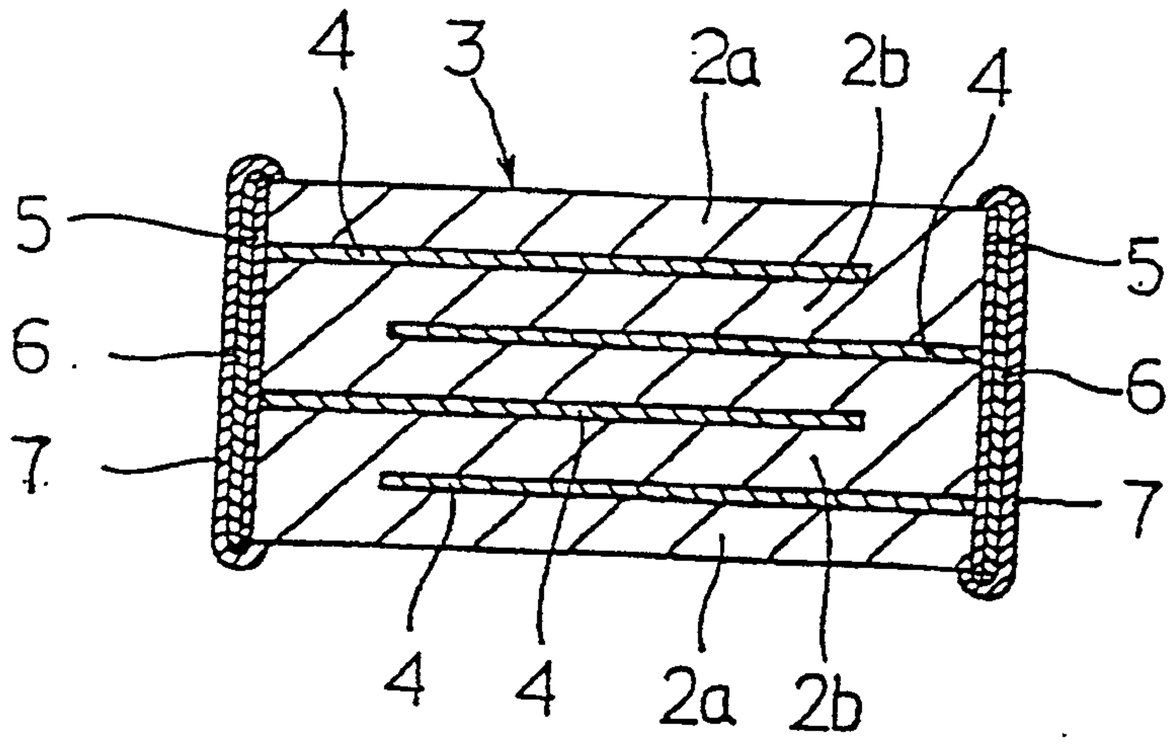


Fig 2

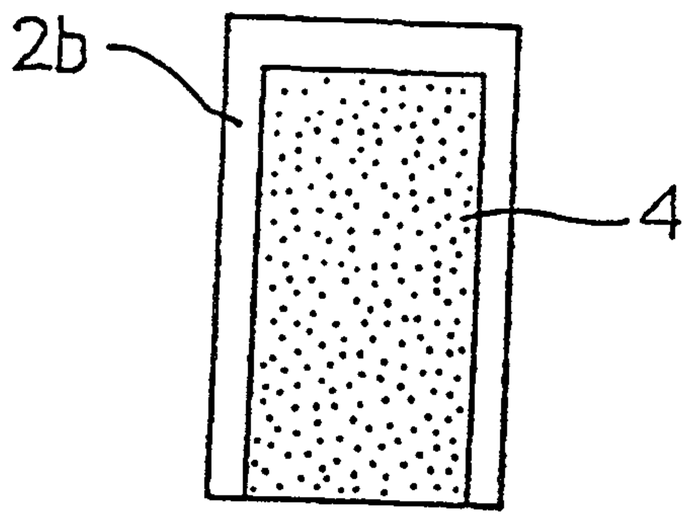
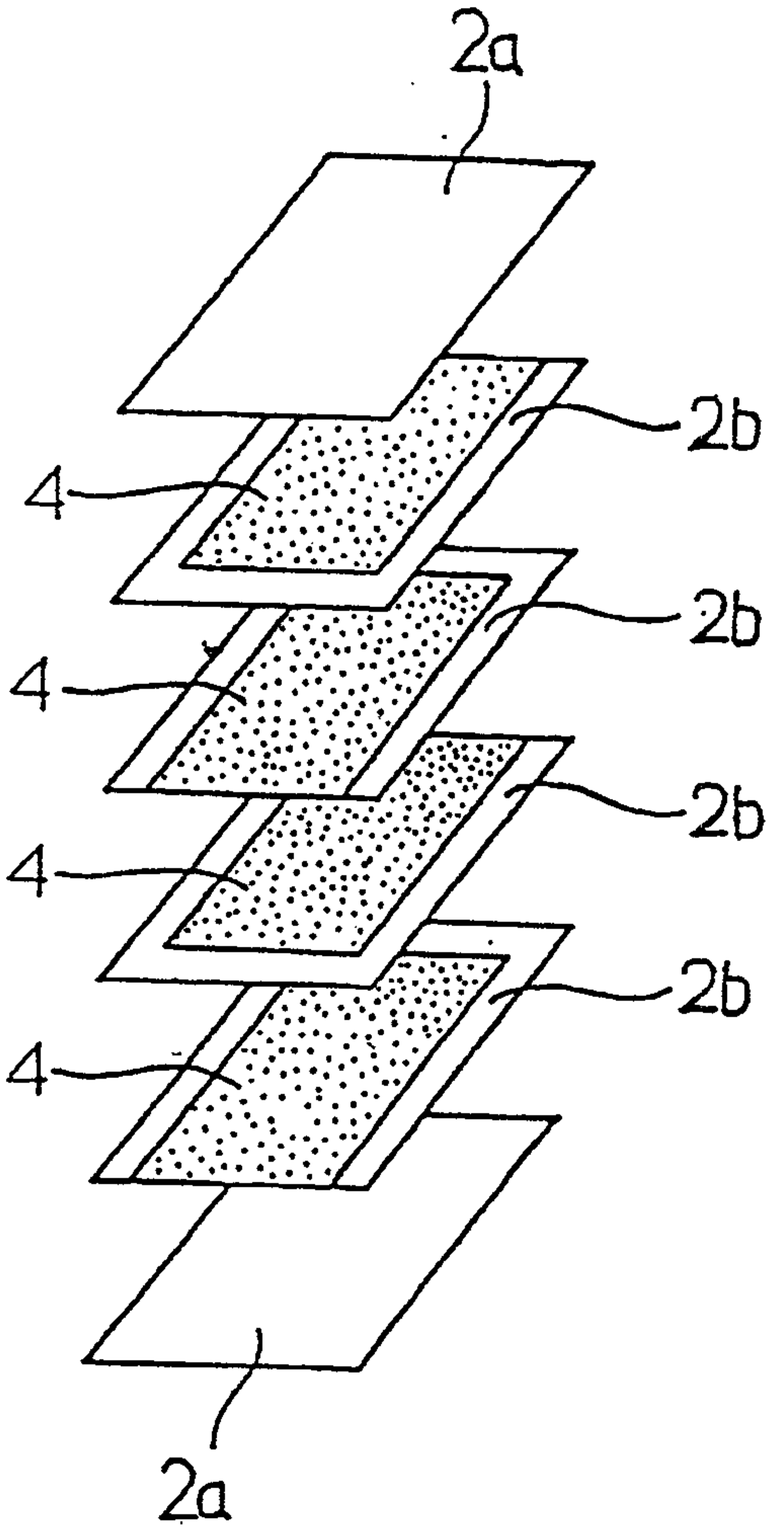
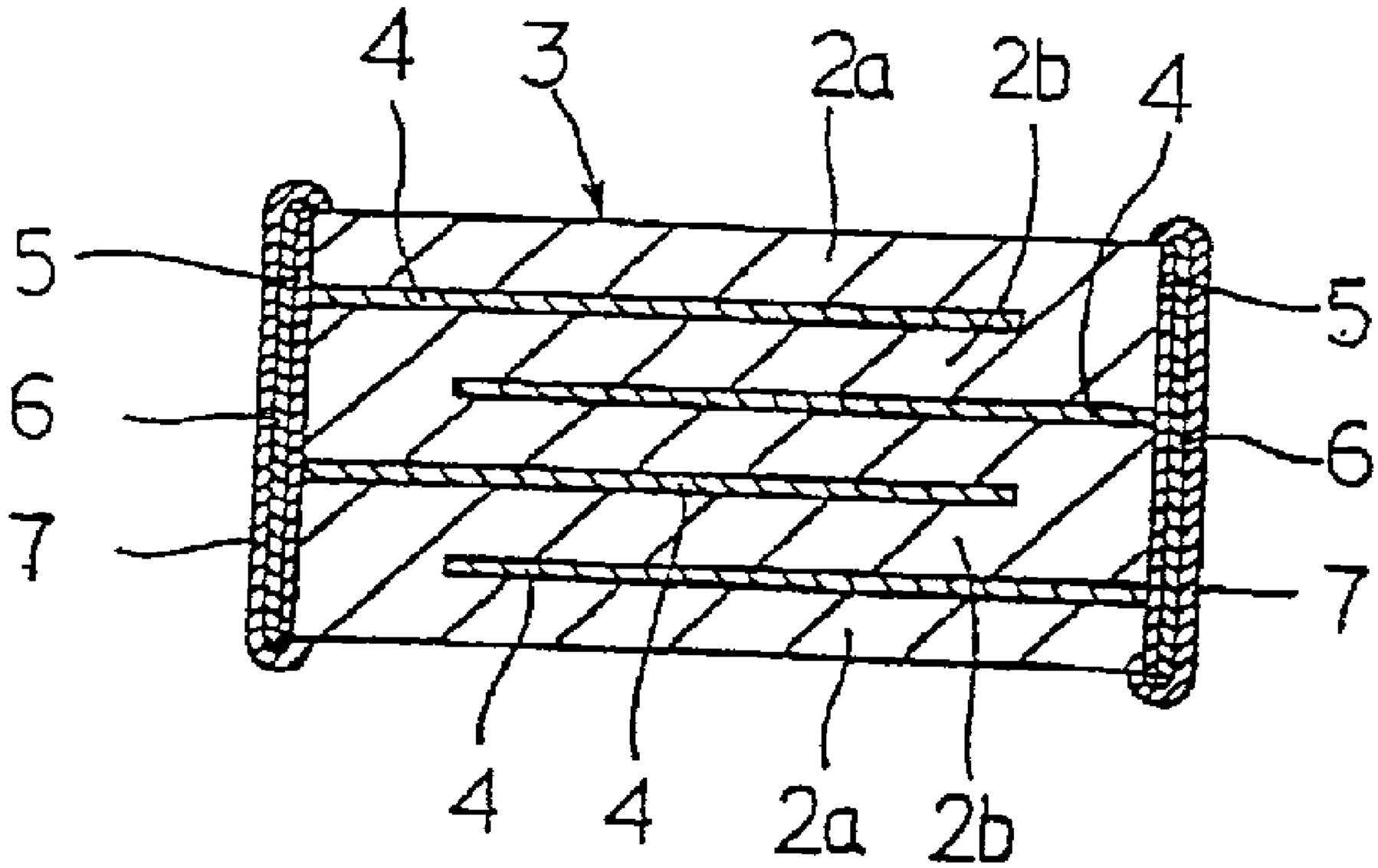


Fig 3

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