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DIELECTRIC CERAMICS COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a dielectric ceramics composition and, more particularly, to the one which is used as a raw material for laminated ceramics capacitors.

2. Description of the Related Art:

A dielectric ceramics compound based on barium titanate (BaTiO_3) has been in general practical use. However, it suffers the disadvantage of requiring firing at high temperatures (usually 1300-1400°C). When used for laminated capacitors, it needs internal electrodes of expensive precious metal (such as platinum and palladium) which withstand the high firing temperature. This leads to high production cost. Therefore, the cost reduction of laminated ceramics capacitor needs a dielectric ceramics composition capable of firing at low temperatures so that inexpensive metals (based on silver and nickel) can be used for the internal electrodes.

Basic electrical properties required of dielectric ceramics compositions include high permittivity, low di-

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electric loss, and high insulation resistance. In addition, high mechanical strength is another requirement for dielectric ceramics compositions. This is true particularly in the case where they are used for laminated chip capacitors, which are subject to mechanical strain when mounted on a substrate because of difference in thermal expansion between the substrate and the dielectric ceramics composition constituting chip capacitors. Such strain causes cracking and damage to chip capacitors. Thus, chip capacitors depend for their reliability on the mechanical properties of the dielectric ceramics composition from which they are made.

Such being the case, there has been a demand for development of a dielectric ceramics composition which is capable of sintering at low temperatures and is superior in mechanical strength.

Japanese Patent Laid-open No. 21850/1980 discloses a dielectric ceramics composition capable of sintering at low temperatures, which is a two-component composition composed of $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ and PbZrO_3 . This composition, however, has a high dielectric loss and a low specific resistance, which are to be remedied. To overcome these

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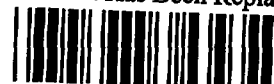
disadvantages, there has been proposed a three-component composition containing $\text{Pb}(\text{Mn}_{2/3}\text{W}_{1/3})\text{O}_3$ as a third component. (Japanese Patent Laid-open No. 23058/1980) This three-component composition, however, is poor in flexural strength and hence is used only for laminated capacitors with limited use. Another ternary dielectric ceramics composition composed of $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$, and PbTiO_3 has been disclosed in Japanese Patent Laid-open No. 60670/1983. In common with the above-mentioned dielectric ceramics composition, it is not satisfactory in mechanical strength.

OBJECT AND SUMMARY OF THE INVENTION

It is an object of the present invention to provide a dielectric ceramics composition which can be sintered at low temperatures and has a high permittivity and sufficient mechanical strength.

The gist of the present invention resides in a dielectric ceramics composition composed mainly of lead magnesium-niobate [$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$], strontium titanate [SrTiO_3], and lead titanate [PbTiO_3], characterized in that the molar ratio of said three major components is defined by $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]_x \cdot [\text{SrTiO}_3]_y \cdot [\text{PbTiO}_3]_z$

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(where $x + y + z = 100$ parts by mole, and each value of x , y , and z is on lines or within the area enclosed by lines passing through four points A (72, 10, 18), B (76, 5, 19), C (57, 5, 38), and D (48, 20, 32) in triangular coordinates), and said three major components are supplemented by $(\text{Pb}_{1-x}\text{Ba}_x)(\text{Cu}_{1/2}\text{W}_{1/2})\text{O}_3$ (where $0 \leq x \leq 1$) in an amount less than 5 parts by mole (excluding 0 part by mole) for 100 parts by mole of said major components.

The dielectric ceramics composition of the present invention can be sintered at low temperatures and has good dielectric properties and high mechanical strength which has never been achieved. It has a flexural strength higher than 120 MPa. Because of this high strength, it will find use as a raw material for laminated chip capacitors. Some samples in this invention have a flexural strength higher than 130 MPa and a relative permittivity higher than 9000 and meet the D characteristics prescribed in JIS.

These and other objects and advantages of the invention may be readily ascertained by referring to the following description and appended drawing.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram showing in triangular coordinates the ratio of major three components in each sample given in Table 1.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Each sample was prepared from Pb_3O_4 , MgO , Nb_2O_5 , TiO_2 , $SrCO_3$, CuO , and WO_3 (technical grade) as starting materials. They were weighed such that the composition shown in Table 1 was established. They were mixed by ball-milling in deionized water (as a solvent) for 16 hours. The resulting powder was calcined in the atmosphere at $750^{\circ}C$ for 2 hours. The calcined powder was mixed with an organic solvent (such as toluene), a binder (such as PVB), and a plasticizer (such as DOP) to give a slurry. The slurry was formed into a green sheet (50-60 μm thick) by the doctor blade method. The green sheet was fabricated into a discoid specimen (1.0 mm thick, 10 mm in diameter) and a rectangular parallelepipedic specimen (45 mm long, 5 mm wide, 1.5 mm thick). These specimens were freed of binder in the atmosphere and then fired in the atmosphere at $950-1100^{\circ}C$. Thus there were obtained the desired ceramics samples.

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Table 1

Sample No.	Composition (parts by mole)				Flexural strength σ (m value)	Relative permittivity	TCC (%)	
	PMN	ST	PT	PBCW			-25°C	85°C
1 *	80	0	20	5	98 (8.3)	4800	-25.7	111
2 *	76	5	19	5	131 (4.3)	11300	-43.8	-13.3
3	72	10	18	5	135 (6.4)	8400	-16.6	-49.7
4	74.4	7	18.6	5	132 (6.8)	9400	-29.5	-28.2
5 *	60	0	40	5	92 (12.6)	2100	-14.7	36
6	57	5	38	5	129 (11.8)	2800	-21	53.7
7	54	10	36	5	128 (7.9)	3500	-23.4	97.8
8	51	15	34	5	152 (6.4)	5600	-33.6	54.3
9	48	20	32	5	138 (9.9)	4700	1.3	-37.4
10	49.2	18	32.8	5	145 (8.5)	5300	-15.8	7.5
11	63	10	27	5	133 (6.9)	10000	-45	-20
12 *	50	10	40	5	90 (7.4)	3000	-30	90
13 *	60	20	20	5	115 (9.5)	5000	-5	-32
14 *	80	10	10	5	105 (8.3)	11000	-50	-10
15 *	63	10	27	0	not sinterable even at 1200°C			
16 *	63	10	27	10	90 (7.9)	9500	-41	-26
17	63	10	27	5	138 (7.1)	9800	-42	-23
18	63	10	27	5	131 (7.6)	9900	-39	-21

* Samples not conforming to the invention.

PMN : $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$

ST : SrTiO_3

PT : PbTiO_3

PBCW : $(\text{Pb}_{1-x}\text{Ba}_x)(\text{Cu}_{1/2}\text{W}_{1/2})\text{O}_3$

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After coating with silver paste on both sides and baking at 800°C in the atmosphere, the discoid specimen was tested for dielectric properties. The relative permittivity (ϵ_r) was measured at 25°C for the frequency of 1 kHz and the voltage of 1 V (rms). The temperature characteristics of electrostatic capacity (TCC) was expressed in terms of change (%) in the capacity at -25°C and 85°C relative to the capacity at 20°C. The capacity was measured for the frequency of 1 kHz and the voltage of 1 V (rms).

The rectangular specimen was used to measure flexural strength by three-point bending test in the following manner. The specimen is placed on two supports, 30 mm apart, and is bent by advancing the crosshead at a rate of 0.5 mm/min. The flexural strength (σ) is calculated from the formula below.

$$\sigma = 3 \times P \times L/2 \times W \times t^2$$

where P : breaking load

L : distance between supports

W : width of the specimen

t : thickness of the specimen

The value of flexural strength is an average of 15-20 measurements calculated from Weibull distribution.



The flexural strength and dielectric properties of the specimens are summarized in Table 1.

Samples Nos. 1 to 16 contain PBCW in which $x = 0$. Sample No. 17 contains PBCW in which $x = 0.5$. Sample No. 18 contains PBCW in which $x = 1$.

The flexural strength (σ) is expressed in terms of MPa, and "m value" is obtained from the Weibull distribution.

The composition of each sample is plotted in the triangular coordinates (Fig. 1). Numerals in the triangular coordinates correspond to the sample numbers.

According to the present invention, the composition is specified as mentioned above. The reason for this is explained with reference to Table 1 and Fig. 1.

Compositions which are plotted under the line B-C give rise to a flexural strength lower than 100 MPa, as in samples Nos. 1 and 5.

Compositions which are plotted outside the lines C-D and A-B give rise to flexural strengths of 90 MPa and 105 MPa as in samples Nos. 12 and 14. Such values are similar to those of conventional lead-based dielectric ceramics compositions.



Compositions which are plotted above the line D-A give rise to a flexural strength of 115 MPa, as in sample No. 13. This value is not enough for the present invention. In the case where the auxiliary component is not added, as in sample No. 15, the sample cannot be sintered even at 1200°C. In other words, the sample does not take on the property that the lead-based dielectric ceramics composition can be sintered at low temperatures. In the case where the auxiliary component is added in an excess amount (more than 5 parts by mole), as in sample No. 16, the sample is extremely poor in flexural strength (90 MPa).

As Table 1 shows, sample No. 4 has a relative permittivity of 9400 and a flexural strength of 132 MPa and sample No. 10 has a relative permittivity of 5300 and a flexural strength of 145 MPa. Moreover, the values of TCC suggest that both samples satisfy the D characteristics prescribed in JIS. This is noteworthy in view of the fact that there have never been conventional lead-based dielectric ceramics compositions which exhibit such high performance.





WHAT IS CLAIMED IS:

1. A dielectric ceramics composition composed mainly of lead magnesium-niobate $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$, strontium titanate $[\text{SrTiO}_3]$, and lead titanate $[\text{PbTiO}_3]$, characterized in that the molar ratio of said three major components is defined by $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]_x \cdot [\text{SrTiO}_3]_y \cdot [\text{PbTiO}_3]_z$ (where $x + y + z = 100$ parts by mole, and each value of x , y , and z is on lines or within the area enclosed by lines passing through four points A (72, 10, 18), B (76, 5, 19), C (57, 5, 38), and D (48, 20, 32) in triangular coordinates), and said three major components are supplemented by $(\text{Pb}_{1-x}\text{Ba}_x)(\text{Cu}_{1/2}\text{W}_{1/2})\text{O}_3$ (where $0 \leq x \leq 1$) in an amount less than 5 parts by mole (excluding 0 part by mole) for 100 parts by mole of said major components.

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