

- [54] **BARIUM TITANATE BASE CERAMIC COMPOSITION HAVING A HIGH DIELECTRIC CONSTANT**
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2,980,546	4/1961	Plessner et al.	106/73.31
3,373,120	3/1968	Nitta et al.	106/73.32 X
3,473,958	10/1969	Waku	106/73.31 X
3,474,043	10/1969	Andersen et al.	106/73.31 X
3,523,028	8/1970	Prokopowicz	106/73.31
3,529,978	9/1970	Taylor et al.	106/73.31
3,586,642	6/1971	Matsuo et al.	106/73.32 X
3,666,505	5/1972	Hoffmann et al.	106/73.32 X
3,788,867	1/1974	Rutt	106/73.31
3,975,307	8/1976	Matsuo et al.	106/73.32 X

Related U.S. Patent Documents

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- [52] U.S. Cl. **106/73.32; 106/73.31; 252/520**
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[56] **References Cited**

U.S. PATENT DOCUMENTS

2,331,444	10/1943	Wainer	106/73.32 X
2,836,501	5/1958	Crownover	106/73.32

FOREIGN PATENT DOCUMENTS

755,860	8/1956	United Kingdom	106/46
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OTHER PUBLICATIONS

"Three -Step Positive Temperature Coefficient of Resistivity....," Kuwabara et al., CA 79:71231t (1973).

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[57] **ABSTRACT**

A ceramic composition having a high dielectric constant which has good stability with temperature variation and the passage of time includes BaTiO₃ in which the molecular ratio of Ba to Ti ranges from about 0.9 to 1.1 as the basic constituent and about 0.1 to 10 mol % of at least one compound selected from the group of Nb₂O₅ and Ta₂O₅ and about 0.01 to 15 mol % of at least one compound selected from the group consisting of In₂O₃, Ga₂O₃, Tl₂O₃, MgO, ZnO and NiO as sub constituents.

8 Claims, No Drawings

BARIUM TITANATE BASE CERAMIC COMPOSITION HAVING A HIGH DIELECTRIC CONSTANT

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

BACKGROUND OF THE INVENTION

The present invention relates to ceramic compositions containing BaTiO₃ as the basic composition, and particularly to such ceramic compositions having a high dielectric constant and in which the dielectric constant remains substantially stable despite temperature variation and the passage of time.

Ceramic compositions having the above described properties are suitable for use in various electronic devices, such as for instance ceramic capacitors. In order to be practical for use in ceramic capacitors, it is desirable that a material have a dielectric constant (ϵ) of up to 2,000. The dielectric constant should remain relatively stable over a wide temperature range, for example, from minus 55° C to plus 125° C and should have good stability over the passage of time. It is also desirable that the dielectric loss ($\tan\delta$) of the material be low.

In order to fulfill these requirements, a variety of compositions have heretofore been prepared. Most of these prior art compositions, however, have only had a dielectric constant which was stable with reference to either temperature or time. Moreover, the temperature range of good dielectric constant stability has been very narrow, so that practical applications have been quite limited.

It has been recently found that ceramic compositions containing barium titanate (BaTiO₃) as the basic component and Ce, La and Bi as additives have a good temperature stability of their dielectric constant over a temperature range of -55° C to +125° C. The stability of the dielectric constant of such materials is also good with respect to time. This fact is reported in detail, for example, by Johannes Just, in an article entitled "Eigenschaften von hochtemperaturbestandigen Sonderkeramiken mit hoher Dielektrizitätskonstante," which appeared in 'Technische Mitteilungen AEG-Telefunken Gesellschaft', Vol. 60, No. 2, pages 125-126 (1970). However, in compositions of the type described in this article having dielectric constants which have good stability with respect to time and temperature, the dielectric constant is degraded to below 1,000 in value. Moreover, since Bi which has a high vapor pressure and is very reactive is contained in these compositions, it is difficult to use them in the manufacture of ceramics. When for instance these compositions are used to manufacture a laminated ceramic capacitor, internal electrodes made of platinum or palladium are noticeably corroded.

An object of the present invention is to eliminate the disadvantages mentioned above.

Another object of the present invention is to provide ceramic compositions which have a high dielectric constant and exhibit good temperature stability over a wide temperature range together with good time stability.

A further object of the present invention is to provide ceramic compositions which contain BaTiO₃ as a basic composition but contain no Bi, so that capacitor manufacture using these compositions is facilitated and these compositions provide an optimum material for the manufacture of, for instance, laminated ceramic capacitors.

SUMMARY OF THE INVENTION

The ceramic compositions of the present invention contain BaTiO₃ as the basic constituent, in which the molecular ratio of Ba to Ti is within the range from about 0.9 to 1.1. These compositions further contain about 0.1 to 10 mol % of at least one compound selected from the group consisting of Nb₂O₅ and Ta₂O₅ and about 0.01 to 15 mol % of at least one compound selected from the group consisting of In₂O₃, Ga₂O₃, Tl₂O₃, MgO, ZnO, and NiO as sub constituents. If desired, compositions within the above composition ranges may also contain about 0.01 to 10 mol % of Al₂O₃ as another sub constituent to provide even greater improvement in both the temperature stability and the time stability of the dielectric constant.

DESCRIPTION OF THE INVENTION

The ceramic compositions of the present invention have BaTiO₃ as their basic constituent. The BaTiO₃ is manufactured so that the molecular ratio of Ba to Ti is within the range of about 0.9 to 1.1. In addition, these ceramic compositions contain about 0.1 to 10 mol % of at least one of Nb₂O₅ and Ta₂O₅ and about 0.01 to 15 mol % of at least one of In₂O₃, Ga₂O₃, Tl₂O₃, MgO, ZnO, and NiO as sub constituents. These compositions may also contain about 0.01 to 10 mol % of Al₂O₃ as a further sub constituent.

If the content of Nb₂O₅ and/or Ta₂O₅ is less than 0.1 mol % in these ceramic compositions, $\tan\delta$ will become large. While, if the content of Nb₂O₅ and/or Ta₂O₅ is more than 10 mol % or if the content of one or more of In₂O₃, Ga₂O₃, Tl₂O₃, MgO, ZnO and NiO is less than 0.01 mol %, the temperature stability of the dielectric constant will be [degraded] *degraded*. If the content of one or more of In₂O₃, Ga₂O₃, Tl₂O₃, MgO, ZnO and NiO is more than 15 mol % or if the content of Al₂O₃ is more than 10 mol %, the value of the dielectric constant will become low, e.g., below 1,500.

According to a first example of the present invention, a ceramic composition is made containing BaTiO₃, about 0.1 to 10 mol % and preferably about 0.5 to 5.0 mol %, of Nb₂O₅ and/or Ta₂O₅ and about 0.01 to 15 mol % and preferably about 0.05 to 5.0 mol % of at least one of In₂O₃, Ga₂O₃, and Tl₂O₃. Less than 10 mol %, and preferably about 0.5 to 5.0 mol % Al₂O₃ may be added to the composition. It is preferable that the total amount of sub constituents in the composition be about 1.05 to 10 mol %.

According to a second example of the present invention, a ceramic composition contains BaTiO₃, about 0.1 to 10 mol % and preferably about 0.5 to 5.0 mol % of Nb₂O₅ and/or Ta₂O₅, about 0.001 to 10 mol % and preferably about 0.5 to 5.0 mol % of MgO, ZnO, or NiO, and about 0.1 to 10 mol % and preferably about 0.5 to 5.0 mol % of Al₂O₃. This composition may also contain at least one of TiO₂, SiO₂, SnO₂, GeO₂ and ZrO₂ in an amount of about 0.01 to 10 mol % and preferably about 0.1 to 5.0 mol %. It is preferable that the total amount of subconstituents in the composition be about 1.6 to 10.0 mol %.

The ceramic compositions of the present invention have a high dielectric constant which is for example in the range of 1,500 to 3,500. The dielectric constant of these compositions has good stability over a wide temperature range, varying only in the range of +15% to -20% over a temperature range of -55° C to +125° C. The dielectric constant of these compositions also has good stability with respect to time.

As starting materials for making the basic constituent of the ceramic compositions of the present invention, BaCO₃ and TiO₂ powders of at least 99% purity were used. Powders of Nb₂O₅, Ta₂O₅, In₂O₃, Ga₂O₃, Tl₂O₃, Al₂O₃, MgO, ZnO, NiO, TiO₂, SnO₂, SiO₂, GeO₂, and ZrO₂ of at least 99% purity were employed as the subconstituents. The BaCO₃ and TiO₂ were added together in equal mols, and were mixed by means of a ball mill. This mixture was thereafter pre-sintered at 1,000° to 1,200° C. It was determined by the powder X-ray diffraction method that the pre-sintering caused the powder to be thoroughly transformed into BaTiO₃. The pre-sintered BaTiO₃ powder and the starting materials of subconstituents were weighed to obtain the necessary quantities, and were mixed by means of a ball mill. After filtration and drying, the mixture was pressure-molded into discs having a diameter of 16mm. These discs were sintered then at 1,300° to 1,450° C for 1 hour.

Silver electrodes were then provided on both the principal surfaces of the resultant ceramic discs by burning at 600° C. The dielectric constant (ε) and the dielectric loss (tanδ) were then measured with a capacitance bridge by applying an alternating current of 1 KHz to the ceramic discs at a temperature of 20° C. The temperature stability of the dielectric constant was estimated by measuring it at various temperatures within the

range of -55° C and +125° C and calculating the rate of temperature variation of the dielectric constant with reference to the value of the dielectric constant at +20° C. The temperature stability of the dielectric constant can then be represented by:

$$\frac{\epsilon_{max} - \epsilon_{20}}{\epsilon_{20}} \times 100 \text{ to } \frac{\epsilon_{min} - \epsilon_{20}}{\epsilon_{20}} \times 100,$$

where ε₂₀ denotes the value of ε at +20° C, while ε_{max} and ε_{min} respectively denote the maximum and the minimum values of the dielectric constant within the temperature range of -55° C to +125° C.

In order to estimate the time stability of the dielectric constant, the value of the dielectric constant was measured several times over a period of time from 12 hours to 1,000 hours after the provision of the silver electrodes by burning. The rate of variation (A_t) of the dielectric constant with respect to time was calculated by the following equation:

$$\frac{\epsilon_t - \epsilon_{10}}{\epsilon_{10}} \times 100 = A_t \cdot \log \left(\frac{t}{12} \right),$$

where

t: elapsed time,

ε₁₀: the value of ε at a time 12 hours after the provision of the electrodes by burning, and ε_t: the value of ε after an elapsed time of t hours.

Typical examples of the results obtained are listed in Tables 1, 2 and 3. Specimens shown with an asterisk in the tables are compositions outside the scope of the present invention.

Table 1

Specimen No.	Composition (mol %)						ε [20° C]	tan δ [20° C]	rate of temp. variation of ε (%) [-55° C to +125° C]	rate of time variation of ε [A] (%/decade)		
	BaTiO ₃	Nb ₂ O ₅	Al ₂ O ₃	Other Subconstituents								
1*	95	2.5	2.5	—	—	—	3130	6.40	+4	~ -42	-1.5	
2*	96	2.5	1.5	—	—	—	2310	0.78	+19	~ -30	-1.0	
3*	96.5	1.5	2.0	—	—	—	2770	0.36	0	~ -40	-0.8	
4	96	1.5	2.49	In ₂ O ₃	0.01	—	2540	0.45	0	~ -19	-0.8	
5	96	1.5	2.40	"	0.10	—	2450	0.40	0	~ -16	-1.2	
6	96	1.5	2.25	"	0.25	—	2040	0.35	+1	~ -8	-1.2	
7	96	1.5	2.00	"	0.50	—	2270	0.55	+15	~ -10	-1.0	
8	96	1.5	1.50	"	1.00	—	1820	0.55	+15	~ -10	-1.5	
9	97	1.0	—	"	2.0	—	2620	0.40	0	~ -16	-1.1	
10	99.79	0.1	0.1	"	0.1	—	2510	1.92	+7	~ -11	-1.8	
11	84.8	10.0	5.0	"	0.2	—	1980	0.98	+10	~ -6	-0.7	
12	77.5	5.0	2.5	"	15.0	—	1750	0.48	+9	~ -19	-0.8	
13	92.5	2.0	5.0	"	0.5	—	1510	0.36	+8	~ -6	-1.3	
14	96.7	2.0	1.0	"	0.3	—	3000	0.33	+4	~ -9	-1.2	
15	97.8	1.5	0.5	"	0.2	—	3100	0.41	+8	~ -10	-1.0	
16	78.0	7.0	—	Ga ₂ O ₃	15.0	—	1770	0.86	+12	~ -18	-1.0	
17	97.2	1.5	1.0	"	0.3	—	2200	0.42	+4	~ -10	-1.2	
18	97.2	1.5	1.2	"	0.1	—	2460	0.67	0	~ -17	-0.8	
19	78.0	7.0	—	Tl ₂ O ₃	15.0	—	1650	0.79	+11	~ -18	-0.9	
20	97.2	1.5	1.0	"	0.3	—	2110	0.51	+8	~ -6	-1.3	
21	97.2	1.5	1.2	"	0.1	—	2300	0.39	0	~ -13	-1.0	
22	94.0	2.5	3.0	MgO	0.5	—	2500	0.51	+14	~ -12	-1.5	
23	79.8	0.1	0.1	"	10.00	TiO ₂	10.0	3000	2.10	+5	~ -15	-0.7
24	83.0	10.0	5.0	"	1.0	"	1.0	2530	1.00	+13	~ -14	-1.0
25	83.0	5.0	10.0	"	1.0	"	1.0	2100	0.89	+12	~ -13	-1.2
26	97.98	1.0	1.0	"	0.01	"	0.01	2300	0.43	+13	~ -15	-1.5
27	95.0	2.5	1.5	"	0.5	"	0.5	1860	0.45	+10	~ -13	-1.5
28	95.0	2.0	2.0	"	0.5	"	0.5	2560	0.50	+12	~ -9	-1.2
29	94.5	1.0	1.5	"	1.5	"	1.5	1820	0.60	+17	~ -12	-1.0
30	97.99	1.0	1.0	ZnO	0.01	—	—	2400	0.83	+4	~ -13	-1.3
31	93.0	1.0	1.0	ZnO	2.5	TiO ₂	2.5	2750	0.90	+6	~ -13	-1.0
32	92.0	1.0	1.0	"	3.0	"	3.0	2530	1.10	+5	~ -12	-2.0
33	78.0	1.0	1.0	"	10.0	"	10.0	1650	0.53	+7	~ -11	-1.0
34	93.5	2.5	2.0	"	1.0	SnO ₂	1.0	2300	0.73	+9	~ -10	-1.5
35	78.0	1.0	1.0	"	10.0	"	10.0	1700	0.62	+3	~ -7	-1.4
36	95.5	1.0	1.5	"	1.0	SiO ₂	1.0	2400	0.65	+7	~ -8	-0.9
37	78.0	1.0	1.0	"	10.0	"	10.0	1730	0.55	+9	~ -4	-0.7
38	95.5	1.0	1.5	"	1.0	GeO ₂	1.0	2630	0.43	+10	~ -7	-1.3
39	78.0	1.0	1.0	"	10.0	"	10.0	1560	0.41	+3	~ -6	-2.0

Table 1-continued

Specimen No.	Composition (mol %)					ε [20° C]	tan δ (%) [20° C]	rate of temp. variation of ε (%) [-55° C to +125° C]	rate of time variation of ε [A.] (%/decade)			
	BaTiO ₃	Nb ₂ O ₅	Al ₂ O ₃	Other Subconstituents								
40	94.5	2.0	1.5	"	1.0	ZrO ₂	1.0	2120	0.81	+4	~ -10	-1.7
41	78.0	1.0	1.0	"	10.0	"	10.0	1770	0.91	+7	~ -9	-2.0
42	97.0	1.0	1.5	NiO	0.5	"	"	2440	0.83	+3	~ -11	-0.7
43	95.98	2.0	2.0	"	0.01	TiO ₂	0.01	2510	0.75	+4	~ -9	-1.2
44	95.0	1.5	1.5	"	1.0	"	1.0	2320	0.91	+7	~ -7	-1.3
45	78.0	1.0	1.0	"	10.0	"	10.0	1600	1.01	+11	~ -4	-1.1
46	97.99	1.0	1.0	In ₂ O ₃	0.005	Ga ₂ O ₃	0.005	2830	0.35	+1	~ -13	-0.7
47	97.90	1.0	1.0	"	0.05	"	0.05	2540	0.41	+3	~ -11	-1.1
48	97.75	1.0	1.0	"	0.125	"	0.125	2500	0.35	+5	~ -10	-1.2
49	97.50	1.0	1.0	"	0.25	"	0.25	2380	0.51	+8	~ -9	-0.9
50	97.00	1.0	1.0	"	0.5	"	0.5	2320	0.72	+10	~ -5	-0.8
51	97.00	1.0	"	"	1.0	"	1.0	2330	0.63	+5	~ -8	-1.0
52	99.79	0.01	0.1	"	0.05	"	0.05	2960	0.91	+4	~ -10	-1.3
53	88.80	10.0	1.0	"	0.1	"	0.1	1820	0.21	+1	~ -13	-0.7
54	83.90	1.0	0.1	"	7.5	"	7.5	1550	0.32	+7	~ -11	-0.9
55	88.50	1.0	10.0	"	0.25	"	0.25	1920	0.43	+5	~ -10	-0.8
56	97.70	1.5	0.5	"	0.15	"	0.15	2480	0.38	+8	~ -7	-0.9
57	84.00	1.0	"	Tl ₂ O ₃	7.5	"	7.5	1630	0.55	+3	~ -14	-1.1
58	97.20	1.5	1.0	"	0.15	"	0.15	2210	0.61	+9	~ -7	-1.2
59	97.29	1.5	1.2	"	0.005	"	0.005	2350	0.48	+2	~ -12	-0.7
60	84.00	1.0	"	"	7.5	In ₂ O ₃	7.5	1610	0.65	+5	~ -13	-0.9
61	97.20	1.5	1.0	"	0.15	"	0.15	2280	0.54	+7	~ -9	-0.8
62	97.29	1.5	1.2	Tl ₂ O ₃	0.005	In ₂ O ₃	0.005	2310	0.37	+4	~ -9	-1.1
63	92.00	1.0	"	Ga ₂ O ₃	2.0	"	3.0	2120	0.71	0	~ -15	-1.0
				Ga ₂ O ₃	2.0	"	"	"	"	"	"	"
64	97.20	1.5	1.0	Tl ₂ O ₃	0.1	"	0.03	2430	0.62	+11	~ -5	-1.0
				Ga ₂ O ₃	0.17	"	"	"	"	"	"	"
65	97.29	1.5	1.2	Tl ₂ O ₃	0.002	"	0.003	2510	0.53	+3	~ -7	-0.9
				Ga ₂ O ₃	0.005	"	"	"	"	"	"	"

Table 2

Specimen No.	Composition (mol %)						ε [20° C]	tan δ (%) [20° C]	rate of temp. variation of ε (%) [-55° C to +125° C]	rate of time variation of ε [A.] (%/decade)	
	BaTiO ₃	Ta ₂ O ₅	Al ₂ O ₃	In ₂ O ₃	Ga ₂ O ₃	Tl ₂ O ₃					
66*	99.0	1.0	"	"	"	"	2800	4.8	+30	~ -40	-3.0
67	98.99	1.0	0.01	"	"	"	2720	0.64	0	~ -17	-1.0
68	98.0	1.0	1.0	"	"	"	2540	0.35	0	~ -20	-1.6
69	84.0	1.0	1.5	"	"	"	1500	0.82	+11	~ -4	-1.8
70	98.49	1.5	"	0.01	"	"	2380	0.67	0	~ -13	-1.5
71	97.5	1.5	"	1.0	"	"	2300	0.71	+4	~ -3	-1.5
72	84.0	1.0	"	1.5	"	"	1510	0.73	+3	~ -6	-1.7
73	98.49	1.5	"	"	0.01	"	2740	0.61	+4	~ -8	-1.4
74	98.0	1.0	"	"	1.0	"	3190	0.65	+11	~ -4	-2.0
75	84.0	1.0	"	"	1.5	"	1500	0.79	+9	~ -3	-2.1
76	98.49	1.5	"	"	"	0.01	2710	0.84	+5	~ -9	-0.9
77	97.5	1.5	"	"	"	1.0	2650	0.71	+9	~ -10	-1.1
78	84.0	1.0	"	"	"	1.5	1530	0.62	+10	~ -12	-1.3
79	98.87	0.1	1.0	0.03	"	"	2630	0.73	+11	~ -8	-0.8
80	97.5	1.0	1.0	0.5	"	"	2410	0.52	+8	~ -9	-1.1
81	96.47	1.5	2.0	0.03	"	"	2260	0.43	+7	~ -7	-1.5
82	93.9	5.0	1.0	0.1	"	"	2080	0.44	+3	~ -12	-1.6
83	88.9	10.0	1.0	0.1	"	"	1610	0.76	+0	~ -15	-1.8
84	98.0	1.0	0.5	"	0.5	"	2580	0.71	+0	~ -14	-2.0
85	97.5	1.0	1.0	"	"	0.5	2540	0.65	+0	~ -17	-2.1
86	97.5	1.0	"	"	1.0	0.5	2420	0.56	+3	~ -13	-1.3
87	98.0	1.0	"	0.5	"	0.5	2680	0.81	+1	~ -11	-1.2
88	97.5	1.0	"	0.5	1.0	"	2370	0.77	+2	~ -11	-1.5
89	97.47	1.0	"	0.03	1.0	0.5	2330	0.69	+5	~ -9	-1.7
90	97.97	1.0	0.5	"	0.5	0.03	2410	0.53	+4	~ -12	-1.9
91	97.47	1.0	1.0	0.03	"	0.5	2330	0.55	+7	~ -10	-1.1
92	95.95	1.5	1.5	0.05	1.0	"	2150	0.62	+6	~ -9	-0.8
93	96.3	1.5	0.5	0.1	1.5	0.1	2470	0.71	+5	~ -5	-0.6

Table 3

Specimen No.	Composition (mol %)					ε [20° C]	tan δ (%) [20° C]	rate of temp. variation of ε (%) [-55° C to +125° C]	rate of time variation of ε [A.] (%/decade)
	BaTiO ₃	Nb ₂ O ₅	Ta ₂ O ₅	Al ₂ O ₃	In ₂ O ₃				
94	96.0	0.5	1.0	2.25	0.25	2130	0.38	+2 ~ -7	-1.0
95	97.5	0.5	0.5	1.0	0.5	2380	0.45	+6 ~ -7	-0.9
96	96.47	1.0	0.5	2.0	0.03	2280	0.45	+3 ~ -7	-0.8

The specimens numbered 1, 2, 3 and 66 indicate results for compositions outside the scope of the present

invention for comparison. Results for specimens 1, 2, 3 and 66 show wide percentage variation of the dielectric

constant of the test compositions within the range of temperatures tested. By contrast from Tables 1 to 3, the example specimens numbered 4 through 65 and 67 through 96 have compositions within the scope of the present invention, and these compositions show a relatively smaller variation in dielectric constant with variation in temperature. The rate of variation of dielectric constant with time of these compositions is also small. Moreover, the compositions of the present invention have dielectric constants of sufficiently large values and superior values of dielectric loss (tanδ).

While almost all of the foregoing examples have been described as employing, as the basic constituent, BaTiO₃ in which Ba and Ti are used in equimolecular amounts, similar effects can be achieved utilizing BaTiO₃ in which the molecular ratio of Ba to Ti (Ba/Ti) ranges from about 0.9 to 1.1, as shown by the results for specimens 50, 56, 71 and 80 in Tables 1 and 2. The specimens numbered 50 and 71 indicate results for compositions in which the molecular ratio of Ba to Ti (Ba/Ti) is 0.9. While, the specimens 56 and 80 indicate results for compositions in which the molecular ratio of Ba to Ti is 1.1.

We claim:

1. A dielectric ceramic composition having a high dielectric constant, consisting of 77.5 to 99.79 mol % of BaTiO₃, 0.1 to 10 mol % of at least one of Nb₂O₅ and Ta₂O₅, and about 0.01 to 15 mol % of at least one of the compounds In₂O₃, Ga₂O₃, and Tl₂O₃.

2. A dielectric ceramic composition having a high dielectric constant, consisting of 77.5 to 99.79 mol % of BaTiO₃, 0.1 to 10 mol % of at least one of Nb₂O₅ and Ta₂O₅, about 0.01 to 15 mol % of at least one of the compounds In₂O₃, Ga₂O₃, and Tl₂O₃, and about 0.01 to 10 mol % of Al₂O₃.

3. A dielectric ceramic composition, having a high dielectric constant, consisting of 77.5 to 99.79 mol % of BaTiO₃ as a basic constituent, 0.5 to 5.0 mol % of Nb₂O₅ as a sub constituent, and 0.05 to 5.0 mol % of at

least one of the compounds In₂O₃, Ga₂O₃, and Tl₂O₃ as another sub constituent.

4. A dielectric ceramic composition, having a high dielectric constant, consisting of 77.5 to 99.79 mol % of BaTiO₃ as a basic constituent, 0.5 to 5.0 mol % of Nb₂O₅ as one sub constituent, 0.05 to 5.0 mol % of at least one of the compounds In₂O₃, Ga₂O₃, and Tl₂O₃ as a second sub constituent and 0.5 to 5.0 mol % of Al₂O₃ as a third sub constituent, the total amount of said sub constituents being within a range of 1.05 to 10 mol %.

5. A dielectric ceramic composition, having a high dielectric constant, consisting of 77.5 to 99.79 mol % of BaTiO₃ as a basic constituent, 0.5 to 5.0 mol % of Ta₂O₅ as a sub constituent, and 0.05 to 5.0 mol % of at least one of the compounds In₂O₃, Ga₂O₃, and Tl₂O₃ as another sub constituent.

6. A dielectric ceramic composition, having a high dielectric constant, consisting of 77.5 to 99.79 mol % of BaTiO₃ as a basic constituent, 0.5 to 5.0 mol % of Ta₂O₅ as a sub constituent, 0.05 to 5.0 mol % of at least one of the compounds In₂O₃, Ga₂O₃, and Tl₂O₃ as another sub constituent and 0.5 to 5.0 mol % of Al₂O₃ as a further sub constituent.

7. A dielectric ceramic composition, having a high dielectric constant, consisting of 77.5 to 99.79 mol % of non-stoichiometric BaTiO₃ in which the molecular ratio of Ba to Ti lies within the range of approximately 0.9 to 1.1, 0.1 to 10 mol % of at least one of Nb₂O₅ and Ta₂O₅; and 0.01 to 15 mol % of at least one of the compounds In₂O₃, Ga₂O₃ and Tl₂O₃.

8. A dielectric ceramic composition having a high dielectric constant, consisting of 77.5 to 99.79 mol % of non-stoichiometric BaTiO₃ in which the molecular ratio of Ba to Ti lies within the range of approximately 0.9 to 1.1, 0.1 to 10 mol % of at least one of Nb₂O₅ and Ta₂O₅; 0.01 to 15 mol % of at least one of the compounds In₂O₃, Ga₂O₃ and Tl₂O₃; and further including 0.01 to 10 mol % of Al₂O₃.

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