

Throughout the specification,
"mechanical factor of merit" → "mechanical quality factor"

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PIEZOELECTRIC CERAMIC COMPOSITIONS

BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates to piezoelectric ceramic compositions and, more particularly, to piezoelectric ceramic compositions preferably used in ultrasonic motors, ultrasonic vibrators, piezoelectric actuators, and the like.

Description of the Related Art

~~{Piezoelectric}~~ It is preferable that the piezoelectric materials (piezoelectric ceramic compositions) used in ultrasonic motors, ultrasonic vibrators, piezoelectric actuators, and the like ~~{are desired to}~~ have a large mechanical ^{quality factor} ~~factor of merit~~, less heat generation during the application of a high voltage, a large piezoelectric constant, and a large amplitude of vibration.

Further, it is important for piezoelectric materials for ultrasonic motors to have stable temperature characteristics to be able to provide stable speed of rotation and torque.

For conventional piezoelectric ceramic compositions, however, it is difficult to keep both ~~{of}~~ the mechanical factor of merit and the piezoelectric constant sufficiently large, and ~~{it is often the case that}~~ the stability of the temperature characteristics is often not sufficient.

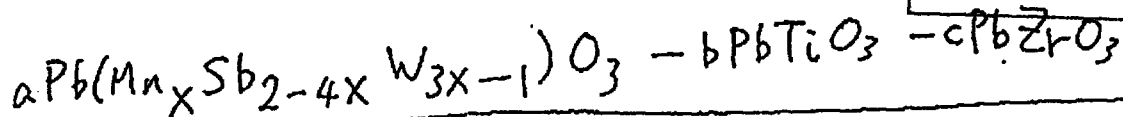
Piezoelectric ceramic compositions prepared to satisfy the above-described requirements as much as possible often have firing temperatures as high as 1200 to 1300 °C.

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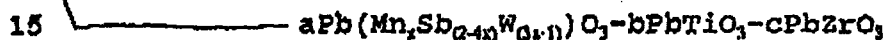
7 general formula

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SUMMARY OF THE INVENTION

The preferred embodiments of the present invention ~~{solves} solve~~ the above-described problems, and ~~{it is an object of the invention to}~~ provide a piezoelectric ceramic composition suitable for use as a material for ultrasonic motors, ultrasonic vibrators, and piezoelectric actuators, ~~{which has} the~~ piezoelectric ceramic composition having a large piezoelectric constant and a large mechanical factor of merit, {is} stable {in} temperature characteristics, and {can be} being adapted to be fired at low temperatures.

According to the preferred embodiments of the present invention, ~~{above-described object is achieved by}~~ a piezoelectric ceramic composition ~~has {characterized in that it is expressed by}~~ a general formula:



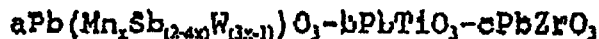
where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$).

According to another aspect of the preferred embodiments of the present invention, ~~{there is provided}~~ a piezoelectric ceramic composition ~~{characterized in that it is obtained by adding}~~ comprises at least one of magnesium, cobalt, and nickel in a ratio of 50 % or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO , NiO , respectively, ~~{to} in a composition {expressed by} having~~ a general formula:



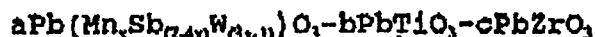
where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$).

According to another aspect of the preferred embodiments of the present invention, there is provided a piezoelectric ceramic composition ~~{characterized in that it is expressed by}~~ having a general formula:



where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$) and in that wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum ~~is substituted for lead by 5 mol % or less~~.

According to still another aspect of the preferred embodiments of the present invention, there is provided a piezoelectric ceramic composition expressed by a general formula:

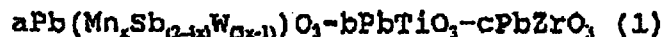


where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$), wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum ~~is substituted for lead by 5 mol % or less, characterized in that it is added with~~ and including at least one of magnesium, cobalt, and nickel in a ratio of 50 % or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO , and NiO .

DETAILED DESCRIPTION OF (THE) PREFERRED EMBODIMENTS

The features of the present invention will now be more specifically described with reference to a preferred ~~embodiment~~ embodiments thereof.

Materials and additives PbO , TiO_2 , ZrO_2 , MnCO_3 , Sb_2O_3 , WO_3 , are weighed to obtain the compositions as shown in Tables 1 through 4 and are subjected to wet mixing using a ball mill with a basic composition expressed by a general formula:



where $a + b + c = 100$, the ratios of x, a, b, and c being varied as shown in Tables 1 through 4. The values of magnesium, cobalt, and nickel in Tables 1 through 4 are the values of added magnesium, cobalt, and nickel compounds in terms of $\text{Mg}(\text{OH})_2$, CoO , and NiO , respectively.



The mixtures obtained as a result of the wet mixing are calcined for two hours at 850 to 950 °C, and the calcined materials are subjected to wet pulverization using a ball mill to obtain conditioned powders.

- 5 The conditioned powders are subjected to press molding after being ~~added~~ combined with water or a binder such as polyvinyl alcohol and are fired for two hours at a temperature of 1100 to 1200 °C.

- 10 Next, the ceramics obtained as a result of the firing are ground to be in the form of a disc having a diameter of about 10 mm and a thickness of about 1 mm, and silver electrodes are applied on both end faces thereof. The ceramics are subjected to a polarization process for 60 minutes in an insulating oil at 80 °C using an electrical field of 3 to 4 KV to obtain
- 15 piezoelectric ceramics.

Tables 1 through 4 show the measured characteristics [measured on] of the piezoelectric ceramics obtained as described above.

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The asterisked samples in Tables 1 through 4 are examples for comparison which are not in accordance with the preferred embodiments of the invention, and other samples are in accordance with the [inventions] preferred embodiments of the present invention.

In ~~[those]~~ tables 1 through 4, d31 represents a piezoelectric constant; Qm represents a mechanical factor of merit; and C-TC represents the temperature coefficient of an electrostatic capacity at -20 to 80 °C.

The piezoelectric characteristics were obtained through calculations ~~[on]~~ of resonance frequencies and antiresonance frequencies measured by an impedance meter (in accordance with Japan Electronic Material Industrial Association Standard (EMAS-6100)). The measurement frequency for the temperature coefficient was 1 KHz.

In a piezoelectric ceramic composition according to the preferred embodiments of the present invention, the ratio of the third component of the basic composition and the ratio between the oxides, i.e., the values of a, b, and c, are defined as described above because ratios ~~[out]~~ outside of this range will give undesirably small piezoelectric constants (d31) and mechanical factors of merit (Qm) and poor temperature coefficients (C-TC). The reasons for such a limitation will be described ~~[below in detail]~~ in the following paragraphs.

An examination ~~[on]~~ of the characteristics of the piezoelectric ceramics (samples) having sample numbers 1 through 23 ~~[on]~~ in Tables 1 and 2 indicates that for the samples (examples for comparison) in which the values of a, b, and c are not in accordance with the preferred embodiments of the present invention, at least ~~[either]~~ one of the piezoelectric constant (d31) and the mechanical factor of merit (Qm) is



extremely small or the temperature coefficient (C-TC) is so large ~~as to deteriorate~~ that the temperature characteristics deteriorate.

Referring to the value a, for example, for a sample
5 whose value a is less than 2 mol %, such as the sample No. 7
on Table 1 (the value a is 1.0 mol % for the sample No. 7)
the piezoelectric constant (d31) and mechanical factor of merit
(Qm) are undesirable. As apparent from the sample No. 17 on
Table 1, for a sample whose value a exceeds 10 mol % (the value a
10 is 12.0 mol % for the sample No. 17), the temperature coefficient
(C-TC) is undesirable ~~as well as~~ and the ~~poor~~ piezoelectric
constant (d31) and mechanical factor of merit (Qm) are poor.

It is therefore preferable that the value a in the
above-described general formula (1) is in the range ~~from~~ of
15 about 2 to 10 mol %. In another preferred embodiment, the range
for a is about 5 to 6 mol %.

Referring to the value b, for example, for a sample
whose value b is less than 40 mol % such as the sample No. 18 on
Table 1 (the value b is 38.0 mol % for the sample No. 18), the
20 piezoelectric constant (d31) and mechanical factor of merit (Qm)
are undesirable. Further, as apparent from the samples No. 22
and No. 23 on Table 2, a sample whose value b exceeds 52 mol %
(the value b is 54.0 mol % and 58.0 mol % for the samples No. 22
and No. 23, respectively) has an undesirable piezoelectric
25 constant (d31).

It is therefore preferable that the value b in the
above-described general formula (1) is in the range ~~from~~ of
30 about 40 to 52 mol %. In another preferred embodiment, the range
for b is about 44 to 50 mol %.

The value c in the above-described general formula (1)
is a value which is automatically determined by the values



a and b because $a + b + c = 100$.

Although no limit is placed on the value x for a piezoelectric ceramic composition according to the preferred embodiments of the present invention, x is preferably in the range from about 35 % to about 48 % (from about 0.35 to 0.48) in order to obtain a practicable piezoelectric ceramic having good characteristics. For example, the piezoelectric ceramic having sample number 1 whose value x is less than 35 % (0.35) is susceptible to warpage and is therefore unpracticable. In another preferred embodiment, the range for x is about 36% to 42% (from about 0.36 to 0.42).

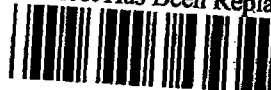
The samples No. 24 through No. 35 on Table 2 are piezoelectric ceramics which have been added with magnesium (magnesium compound) in varying amounts. Those samples indicate that although the addition of magnesium improves the mechanical factor of merit (Q_m), the mechanical factor of merit (Q_m) is conversely reduced significantly if the amount of magnesium added exceeds [0.50] 50 % by weight in terms of $Mg(OH)_2$.

The samples No. 36 through No. 40 on Table 2 are piezoelectric ceramics which have been added with cobalt (cobalt compound) in varying amounts. Those samples indicate that the change in characteristics caused by the addition of cobalt has the same tendency as that caused by the addition of magnesium as described above.

The samples No. 41 through No. 45 on Table 2 are piezoelectric ceramics which have been added with nickel (nickel compound) in varying amounts. The change in characteristics caused by the addition of nickel also has the same tendency as that caused by the addition of magnesium as described above.

It is apparent from the samples No. 46 though No. 48 on Table 3 that the addition of two or more of the elements

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magnesium (magnesium compound), cobalt (cobalt compound), and nickel (nickel compound) provides a piezoelectric ceramic having a large piezoelectric constant (d_{31}), a large mechanical factor of merit (Q_m), and good temperature characteristics. As apparent from the sample No. 49 on Table 3, however, the mechanical factor of merit (Q_m) tends to deteriorate significantly when the total amount of the added magnesium, cobalt, and nickel (the sum of the added values in terms of $Mg(OH)_2$, CoO , and NiO) exceeds ~~{0.50}~~ 50 % by weight.

10 It is therefore necessary to adjust the amounts of the added magnesium, cobalt, and nickel in terms of $Mg(OH)_2$, CoO , and NiO , respectively, so that they total at ~~{0.50}~~ 50 % or less by weight.

15 Further, Tables 5 and 6 show characteristics obtained by adding combinations of magnesium and cobalt, magnesium and nickel, cobalt and nickel, and magnesium, cobalt, and nickel. The values of magnesium, cobalt, and nickel shown ~~{on}~~ in Tables 5 and 6 are the values of the added magnesium, cobalt, and nickel compounds in terms of $Mg(OH)_2$, CoO , and NiO , respectively. ~~{on}~~
20 In Tables 5 and 6, the samples having asterisked sample numbers are examples for comparison which are not in accordance with the preferred embodiments of the present invention, and the remaining samples are in accordance with the preferred embodiments of the present invention.

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For simplicity in comparison, the data for the samples No. 46 through No. 49 shown ~~in~~ in Table 3 are duplicated ~~in~~ in Tables 5 and 6.

As apparent from Tables 5 and 6, piezoelectric ceramics
5 having a large piezoelectric constant (d_{31}), a large mechanical factor of merit (Q_m), and good temperature characteristics can be obtained by adding magnesium, cobalt, and nickel in combinations wherein the amounts of those elements in terms of $Mg(OH)_2$, CoO , and NiO , respectively, are in ratios such that they total at
10 ~~{0-50}~~ 50 % or less by weight.

The samples No. 50 through No. 54 on Table 4 are samples wherein calcium is substituted for a part of lead. For the samples wherein the substituted amount is in accordance with the preferred embodiments of the present invention, the
15 mechanical factor of merit (Q_m) is increased while the piezoelectric constant (d_{31}) and temperature coefficient ($C-TC$) are deteriorated when the substituted amount exceeds 5 mol % (sample No. 54). The substitution for lead (i.e., A-site) also provides another advantage in that the degree of sintering is
20 improved.

It is further apparent from the samples No. 55 through No. 70 on Table 4 that the addition of magnesium, cobalt, and nickel to a system in which at least one of calcium, strontium, barium, and lanthanum is substituted for a part of lead, provides
25 the same effect as that available in a system wherein lead is not substituted and that the piezoelectric constant (d_{31}) is improved when the added amounts in terms of $Mg(OH)_2$, CoO , and NiO total at ~~{0-50}~~ 50 % or less by weight.

As apparent from the samples No. 57, 60, and 70, even
30 in a system added with magnesium, cobalt, and nickel as described above, the piezoelectric constant (d_{31}) and temperature

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coefficient (C-TC) are deteriorated when the total amount of substitution with at least one of calcium, strontium, barium, and lanthanum exceeds 5 mol %.

5 It is therefore preferable that the amount of at least one of calcium, strontium, barium, and lanthanum substituted for a part of lead is 5 mol % or less.

10 However, the mechanical factor of merit (Qm) tends to deteriorate even for a sample wherein lead (i.e., A-site) is substituted by 5 mol % or less when the amount of the added magnesium, cobalt, and nickel (the sum of the values of them in terms of $Mg(OH)_2$, CoO, and NiO, respectively) exceeds 0.50 % by weight (see sample No. 64).

15 ~~(Figs.)~~ Tables 7 through 11 show characteristics obtained by various combinations of the addition of the additives magnesium, cobalt, and nickel and the elements for substitution calcium, strontium, barium, and lanthanum. ~~(on)~~ In Tables 7 through 11, the values of magnesium, cobalt, and nickel are the values of the added magnesium, cobalt, and nickel compounds in terms of $Mg(OH)_2$, CoO, and NiO. Further, ~~(on)~~ in Tables 7
20 through 11, the samples having asterisked sample numbers are examples for comparison which are not in accordance with the preferred embodiments of the present invention, and the remaining samples are preferred embodiments in accordance with the preferred embodiments of the present invention.

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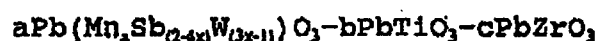


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For simplicity in comparison, the data for the samples No. 50 through No. 70 shown ~~for~~ in Table 4 as described above are duplicated ~~for~~ in Tables 7 through 11.

As apparent from Tables 7 through 11, the combination of the addition of the additives magnesium, cobalt, and nickel and the substitution using the elements calcium, strontium, barium, and lanthanum provides a piezoelectric ceramic having a large piezoelectric constant (d_{31}), a large mechanical factor of merit (Q_m), and good temperature characteristics.

As described above, a piezoelectric ceramic composition according to the preferred embodiments of the present invention expressed by a general formula:



wherein the values (mol %) of a , b , and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively and at least one of magnesium, cobalt, and nickel is added as needed; and at least one of calcium, strontium, barium, and lanthanum is substituted for a part of lead, has a large piezoelectric constant and a large mechanical factor of merit, has stable temperature characteristics, and consistently provides large vibrations even under conditions wherein the temperature fluctuates.

In addition, since it can be fired at a temperature which is about 100 °C lower than that for conventional piezoelectric ceramic compositions, it is possible to obtain a piezoelectric ceramic having good reproducibility by suppressing the vaporization of the lead oxide.

Therefore, a piezoelectric ceramic composition according to the preferred embodiments of the present invention is advantageous especially as a piezoelectric material for ultrasonic motors, ultrasonic vibrators, piezoelectric actuators;

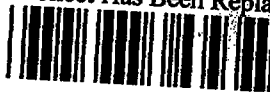
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and the like and is suitable for a variety of industrial purposes.

5 While specific preferred embodiments have been described, it will be appreciated by those skilled in the art that various modifications, changes and additions can be made to the invention without departing from the spirit and scope thereof as set forth in the following claims.

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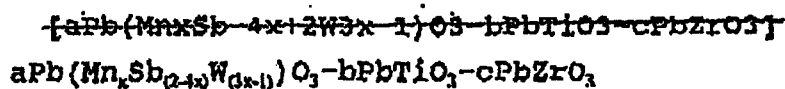


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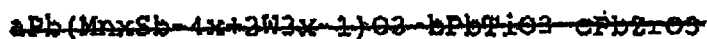
What is claimed is:

1. A piezoelectric ceramic composition expressed by a general formula:



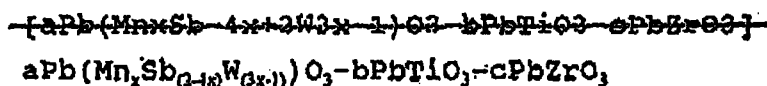
5 where a, b, and c represent mol % and are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$, respectively, ~~[(a, b, and c represent mol %)]~~ and $a + b + c = 100$.

2. A piezoelectric ceramic composition ~~obtained by adding~~ according to claim 1, further comprising at least one of magnesium, cobalt, and nickel in a ratio of ~~50%~~^{0.50%} or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO , NiO to ~~the piezoelectric ceramic composition~~ ~~expressed by a general formula:~~



5 where ~~a, b, and c are in ranges~~ $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$, respectively, ~~(a, b, and c represent mol %, and $a + b + c = 100$)~~.

3. A piezoelectric ceramic composition expressed by a general formula:



5 where a, b, and c represent mol % and are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$, respectively, ~~[(a, b, and c represent mol %)]~~ and $a + b + c = 100$, ~~[in which]~~ wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum ~~[is substituted for lead by 5 mol % or less]~~.

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4. A piezoelectric ceramic composition ~~expressed by a general formula:~~



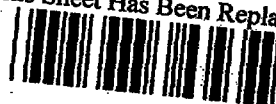
where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and

5 $0.35 \leq x \leq 0.48$, respectively, (a, b, and c represent mol-%, and $a + b + c = 100$), in which, according to claim 3, wherein up to 5% of

lead is replaced by at least one of calcium, strontium, barium, and lanthanum [is substituted for lead by 5 mol-% or less,] and

10 [which is added with] further comprising at least one of magnesium, cobalt, and nickel in a ratio of $\frac{0.50\%}{50\%}$ or less by weight in terms of Mg(OH)_2 , CoO , and NiO .

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Table 1

Sample No.	Composition						Firing Temp (°C)	Characteristics		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)		d ₃₁ (p C/N)	Q _m	C-TC (ppm°C)
1	34.5	6.0	48.0	46.0	—	—	1150	138	1850	2450
2	35.0	6.0	48.0	46.0	—	—	1150	164	1870	1870
3	39.0	6.0	48.0	46.0	—	—	1150	153	1880	1780
4	42.0	6.0	48.0	46.0	—	—	1150	150	1840	1660
5	48.0	6.0	48.0	46.0	—	—	1150	150	1980	1270
6	49.0	6.0	48.0	46.0	—	—	1150	98	2200	1300
7*	42.0	1.0	44.0	55.0	—	—	1150	45	800	1860
8	42.0	2.0	44.0	54.0	—	—	1150	102	1400	2300
9	42.0	2.0	46.0	52.0	—	—	1150	126	1420	1860
10	42.0	2.0	50.0	48.0	—	—	1150	115	2170	1380
11	42.0	5.0	44.0	51.0	—	—	1150	125	2350	2010
12	42.0	5.0	46.0	49.0	—	—	1150	142	2350	1620
13	42.0	5.0	50.0	45.0	—	—	1150	118	2490	1330
14	42.0	10.0	44.0	46.0	—	—	1150	105	1960	3010
15	42.0	10.0	46.0	44.0	—	—	1150	152	1370	2290
16	42.0	10.0	50.0	40.0	—	—	1150	107	2240	1620
17*	42.0	12.0	44.0	44.0	—	—	1150	52	650	3560
18*	36.0	5.0	38.0	57.0	—	—	1150	48	3020	4530
19	36.0	5.0	40.0	55.0	—	—	1150	100	2020	3720
20	36.0	5.0	46.0	49.0	—	—	1150	142	1620	1920

* Examples for comparison according to the prior art



Table 2

Firing

Sample No.	Composition						Burn- Temp (°C)	Characteristics		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)		d ₃₁ (p C/N)	Qm	C-TC (ppm/°C)
21	36.0	5.0	52.0	43.0	—	—	1150	99	2560	1250
22*	36.0	5.0	54.0	41.0	—	—	1150	63	2870	970
23*	36.0	5.0	58.0	37.0	—	—	1150	35	4230	1320
24	42.0	6.0	48.0	46.0	0.10	—	1150	138	3120	1520
25	42.0	6.0	48.0	46.0	0.15	—	1150	150	2500	1420
26	42.0	6.0	46.0	48.0	0.20	—	1150	102	2890	1990
27*	42.0	6.0	48.0	46.0	0.20	—	1150	141	2420	1520
28	42.0	6.0	50.0	44.0	0.20	—	1150	115	2890	1180
29	42.0	6.0	46.0	48.0	0.30	—	1150	109	2920	1930
30	42.0	6.0	48.0	46.0	0.30	—	1150	152	2330	1440
31	42.0	6.0	49.0	45.0	0.30	—	1150	129	2780	1060
32	42.0	6.0	50.0	44.0	0.30	—	1150	114	3000	920
33	42.0	6.0	46.0	48.0	0.50	—	1150	125	1270	1830
34	42.0	6.0	48.0	46.0	0.50	—	1150	148	1160	1420
35*	42.0	6.0	48.0	46.0	0.60	—	1150	165	560	1260
36	42.0	6.0	46.0	48.0	—	0.20	1150	125	2760	1820
37	42.0	6.0	48.0	46.0	—	0.20	1150	156	2330	1430
38	42.0	6.0	50.0	44.0	—	0.20	1150	118	2590	1110
39	42.0	6.0	48.0	46.0	—	0.50	1150	162	1320	1320
40*	42.0	6.0	48.0	46.0	—	0.60	1150	166	690	1210

* Examples for comparison according to the prior art

Table 3

Firing

Sample No.	Composition						Burn Temp (°C)	Characteristics		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)	Ni (% by weight)	ds ₁ (p C/N)	Qm	C-TC (ppm/°C)
41	42.0	6.0	46.0	48.0	—	—	0.20	127	2650	2050
42	42.0	6.0	48.0	46.0	—	—	0.20	148	2210	1330
43	42.0	6.0	50.0	46.0	—	—	0.20	124	1330	1070
44	42.0	6.0	48.0	46.0	—	—	0.50	144	1170	920
45*	42.0	6.0	48.0	46.0	—	—	0.60	155	730	960
46	42.0	5.0	49.0	46.0	0.20	0.10	—	145	2250	1520
47	42.0	5.0	49.0	46.0	0.20	—	0.10	138	2110	1380
48	42.0	5.0	49.0	46.0	0.40	0.10	—	153	1200	1490
49*	42.0	5.0	49.0	46.0	0.50	0.10	—	142	610	1470

* Examples for comparison according to the prior art

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Table 4

Sample No.	Composition						Type and quantity of element to replace Pb (mol %)	Firing Temp (°C)	Characteristic		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)			d ₃₁ (p C/N)	Qm	C-TC (ppm/°C)
50	42.0	6.0	48.0	46.0	—	—	Ca:1	1170	132	2320	1380
51	42.0	6.0	48.0	46.0	—	—	Ca:2	1170	126	2380	1510
52	42.0	6.0	48.0	46.0	—	—	Ca:3	1170	121	2470	1730
53	42.0	6.0	48.0	46.0	—	—	Ca:5	1170	102	2630	2130
54*	42.0	6.0	48.0	46.0	—	—	Ca:6	1170	63	2710	2640
55	42.0	6.0	48.0	46.0	—	—	Sr:2	1170	148	2430	1570
56	42.0	6.0	48.0	46.0	—	—	Sr:5	1170	125	2550	2060
57*	42.0	6.0	48.0	46.0	—	—	Sr:6	1170	69	2590	2560
58	42.0	6.0	48.0	46.0	—	—	Ba:2	1170	145	2320	1530
59	42.0	6.0	48.0	46.0	—	—	Ba:5	1170	120	2560	2070
60*	42.0	6.0	48.0	46.0	—	—	Ba:6	1170	72	2580	2570
61	42.0	6.0	48.0	46.0	—	0.10	Ba:2	1170	129	2120	1520
62	42.0	6.0	48.0	46.0	—	0.20	Ba:2	1170	134	2330	1410
63	42.0	6.0	48.0	46.0	—	0.50	Ba:2	1170	157	1510	1530
64*	42.0	6.0	48.0	46.0	—	0.60	Ba:2	1170	162	780	1580
65	42.0	6.0	48.0	46.0	0.10	—	Ca:1 Sr:1	1170	146	2720	1430
66	42.0	6.0	48.0	46.0	0.10	—	Ca:1 Ba:1	1170	142	2550	1720
67	42.0	6.0	48.0	46.0	0.10	—	Ca:1 La:1	1170	129	2440	1880
68	42.0	6.0	48.0	46.0	0.10	—	Ba:2 La:2	1170	122	2220	2320
69	42.0	6.0	48.0	46.0	0.10	—	Ba:3 La:2	1170	115	1780	2450
70*	42.0	6.0	48.0	46.0	0.10	—	Ba:4 La:2	1170	82	1700	3250

* Examples for comparison according to the prior art



Table 5

Sample No.	Composition						Firing Temp (°C)	Characteristics		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)		ds ₁ (p C/N)	Qm	C-TC (ppm/°C)
101	42.0	5.0	49.0	46.0	0.10	0.10	1190	144	2330	1590
102	42.0	5.0	49.0	46.0	0.10	0.40	1190	152	1160	1480
103*	42.0	5.0	49.0	46.0	0.10	0.50	1190	164	410	1320
104(=46)	42.0	5.0	49.0	46.0	0.20	0.10	1190	145	2250	1520
105	42.0	5.0	49.0	46.0	0.20	0.30	1190	157	1260	1330
106*	42.0	5.0	49.0	46.0	0.20	0.40	1190	163	660	1240
107(=48)	42.0	5.0	49.0	46.0	0.40	0.10	1190	153	1200	1490
108*	42.0	5.0	49.0	46.0	0.40	0.20	1190	159	480	1330
109(=49)*	42.0	5.0	49.0	46.0	0.50	0.10	1190	142	610	1470
110	42.0	5.0	49.0	46.0	0.10	—	1190	129	2010	1560
111	42.0	5.0	49.0	46.0	0.10	—	1190	139	1110	1320
112*	42.0	5.0	49.0	46.0	0.10	—	1190	152	420	1190
113(=47)	42.0	5.0	49.0	46.0	0.20	—	1190	138	2110	1380
114	42.0	5.0	49.0	46.0	0.20	—	1190	144	1020	1310
115*	42.0	5.0	49.0	46.0	0.20	—	1190	151	390	1270
116	42.0	5.0	49.0	46.0	0.40	—	1190	142	1070	1390
117*	42.0	5.0	49.0	46.0	0.40	—	1190	162	520	1220
118*	42.0	5.0	49.0	46.0	0.50	—	1190	164	550	1230
119	42.0	5.0	49.0	46.0	—	0.10	1190	143	2550	1480
120	42.0	5.0	49.0	46.0	—	0.10	1190	155	1230	1380

* Examples for comparison according to the prior art



Table 6

Sample No.	Composition						Finishing Temp (°C)	Characteristics		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)	Ni (% by weight)	d ₃₁ (p C/N)	Qm	C-TC (ppm/°C)
121*	42.0	5.0	49.0	46.0	—	0.10	0.50	167	440	1320
122	42.0	5.0	49.0	46.0	—	0.20	0.10	151	2330	1410
123	42.0	5.0	49.0	46.0	—	0.20	0.30	153	1160	1320
124*	42.0	5.0	49.0	46.0	—	0.20	0.40	159	560	1310
125	42.0	5.0	49.0	46.0	—	0.40	0.10	128	1200	1400
126*	42.0	5.0	49.0	46.0	—	0.40	0.20	149	500	1220
127*	42.0	5.0	49.0	46.0	—	0.50	0.10	157	480	1260
128	42.0	5.0	49.0	46.0	—	0.10	0.10	150	2420	1500
129	42.0	5.0	49.0	46.0	0.10	0.10	0.10	153	1810	1420
130	42.0	5.0	49.0	46.0	0.20	0.20	0.10	157	1230	1370
131*	42.0	5.0	49.0	46.0	0.20	0.10	0.10	168	520	1220
132	42.0	5.0	49.0	46.0	0.40	0.20	0.10	154	1800	1390
133	42.0	5.0	49.0	46.0	0.10	0.20	0.20	158	1330	1360
134*	42.0	5.0	49.0	46.0	0.10	0.40	0.10	172	490	1110
135	42.0	5.0	49.0	46.0	0.10	0.10	0.20	151	1880	1390
136	42.0	5.0	49.0	46.0	0.20	0.10	0.20	152	1090	1320
137*	42.0	5.0	49.0	46.0	0.10	0.10	0.40	154	480	1250

* Examples for comparison according to the prior art



Table 7

Sample No.	Composition						Type and quantity of element to replace Pb (mol %)	Temp (°C)	Characteristic		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)			d ₃₁ (p C/N)	Q _m	C-TC (ppm/°C)
138(=50)	42.0	6.0	48.0	46.0	—	—	Ca:1	1170	132	2320	1380
139(=51)	42.0	6.0	48.0	46.0	—	—	Ca:2	1170	126	2380	1510
140(=52)	42.0	6.0	48.0	46.0	—	—	Ca:3	1170	121	2470	1730
141(=53)	42.0	6.0	48.0	46.0	—	—	Ca:5	1170	102	2630	2130
142(=54*)	42.0	6.0	48.0	46.0	—	—	Ca:6	1170	63	2710	2640
143	42.0	6.0	48.0	46.0	—	—	Sr:1	1170	142	1940	1360
144	42.0	6.0	48.0	46.0	—	—	Sr:5	1170	107	2430	2110
145*	42.0	6.0	48.0	46.0	—	—	Sr:6	1170	74	2600	2530
146	42.0	6.0	48.0	46.0	—	—	Ba:1	1170	138	1970	1400
147	42.0	6.0	48.0	46.0	—	—	Ba:5	1170	104	2540	2120
148*	42.0	6.0	48.0	46.0	—	—	Ba:6	1170	69	2720	2510
149	42.0	6.0	48.0	46.0	—	—	La:1	1170	136	2000	1370
150	42.0	6.0	48.0	46.0	—	—	La:5	1170	105	2510	2010
151*	42.0	6.0	48.0	46.0	—	—	La:6	1170	60	2790	2500
152	42.0	6.0	48.0	46.0	0.10	—	Ba:2	1170	121	3230	1260
153	42.0	6.0	48.0	46.0	0.50	—	Ca:1	1170	130	1460	1180
154*	42.0	6.0	48.0	46.0	0.60	—	Ca:1	1170	145	700	1050
155	42.0	6.0	48.0	46.0	—	0.10	Ca:1	1170	125	3080	1250
156	42.0	6.0	48.0	46.0	—	0.50	Ca:1	1170	143	1660	1100
157*	42.0	6.0	48.0	46.0	—	0.60	Ca:1	1170	146	870	1010

* Examples for comparison according to the prior art



Table 8

Sample No.	Composition						Type and quantity of element to replace Pb (mol %)	Firing Temp (°C)	Characteristic		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)			ds1 (p C/N)	Qm	C-TC (ppm/°C)
158	42.0	6.0	48.0	46.0	—	—	Ca:1	1170	121	3060	1040
159	42.0	6.0	48.0	46.0	—	—	Ca:1	1170	127	1480	860
160*	42.0	6.0	48.0	46.0	—	—	Ca:1	1170	136	790	900
161	42.0	6.0	48.0	46.0	0.10	—	Ca:5	1170	104	3760	1950
162	42.0	6.0	48.0	46.0	0.50	—	Ca:5	1170	111	1360	1820
163*	42.0	6.0	48.0	46.0	0.60	—	Ca:5	1170	122	800	1620
164	42.0	6.0	48.0	46.0	—	0.10	Ca:5	1170	107	3500	1930
165	42.0	6.0	48.0	46.0	—	0.50	Ca:5	1170	120	1590	1700
166*	42.0	6.0	48.0	46.0	—	0.60	Ca:5	1170	123	820	1550
167	42.0	6.0	48.0	46.0	—	—	Ca:5	1170	104	3600	1600
168	42.0	6.0	48.0	46.0	—	—	Ca:5	1170	108	1370	1180
169*	42.0	6.0	48.0	46.0	—	—	Ca:5	1170	115	740	1230
170*	42.0	6.0	48.0	46.0	0.10	—	Ca:6	1170	58	3700	2520
171(-55)	42.0	6.0	48.0	46.0	—	—	Sr:2	1170	148	2430	1570
172	42.0	6.0	48.0	46.0	—	—	Sr:2	1170	152	1330	1480
173*	42.0	6.0	48.0	46.0	—	—	Sr:2	1170	156	710	1460
174(=56)	42.0	6.0	48.0	46.0	—	—	Sr:5	1170	125	2550	2060
175	42.0	6.0	48.0	46.0	—	—	Sr:5	1170	128	1420	1870
176*	42.0	6.0	48.0	46.0	—	—	Sr:5	1170	132	730	1750
177(=57)*	42.0	6.0	48.0	46.0	—	—	Sr:6	1170	69	2590	2560

* Examples for comparison according to the prior art



Table 9

Sample No.	Composition						Type and quantity of element to replace Pb (mol %)	Firing Temp (°C)	Characteristic		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)	Ni (% by weight)		d ₃₁ (p C/N)	Q _m	C-TC (ppm/°C)
178(=61)	42.0	6.0	48.0	46.0	—	0.10	—	1170	129	2120	1520
179(=62)	42.0	6.0	48.0	46.0	—	0.20	—	1170	134	2330	1410
180(=63)	42.0	6.0	48.0	46.0	—	0.50	—	1170	157	1510	1530
181(=64)*	42.0	6.0	48.0	46.0	—	0.60	—	1170	162	780	1580
182(=58)	42.0	6.0	48.0	46.0	—	—	0.20	1170	145	2320	1530
183	42.0	6.0	48.0	46.0	—	—	0.50	1170	151	1280	1400
184*	42.0	6.0	48.0	46.0	—	—	0.60	1170	156	790	1380
185(=59)	42.0	6.0	48.0	46.0	—	—	0.20	1170	120	2560	2070
186	42.0	6.0	48.0	46.0	—	—	0.50	1170	132	1390	1850
187*	42.0	6.0	48.0	46.0	—	—	0.60	1170	136	770	1780
188(=60)*	42.0	6.0	48.0	46.0	—	—	0.20	1170	72	2580	2570
189	42.0	6.0	48.0	46.0	—	—	0.20	1170	145	2330	1630
190	42.0	6.0	48.0	46.0	—	—	0.50	1170	150	1280	1520
191*	42.0	6.0	48.0	46.0	—	—	0.60	1170	152	760	1440
192	42.0	6.0	48.0	46.0	—	—	0.20	1170	122	2470	2130
193	42.0	6.0	48.0	46.0	—	—	0.50	1170	131	1320	1770
194*	42.0	6.0	48.0	46.0	—	—	0.60	1170	139	700	1740
195*	42.0	6.0	48.0	46.0	—	—	0.20	1170	77	2620	2710
196	42.0	6.0	48.0	46.0	0.10	0.10	0.10	1170	132	2850	1250
197	42.0	6.0	48.0	46.0	0.20	0.10	0.10	1170	135	2280	1180

* Examples for comparison according to the prior art



Table 10

Sample No.	Composition						Type and quantity of element to replace Pb (mol %)	Temp (°C)	Characteristic		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)			d ₃₁ (p CN)	Q _m	C-TC (ppm/°C)
198	42.0	6.0	48.0	46.0	0.20	0.20	Ca:1	1170	138	1550	1140
199*	42.0	6.0	48.0	46.0	0.40	0.10	Ca:1	1170	148	660	1010
200	42.0	6.0	48.0	46.0	0.10	0.10	Ca:3	1170	121	3050	1560
201	42.0	6.0	48.0	46.0	0.20	0.10	Ca:3	1170	123	2430	1480
202	42.0	6.0	48.0	46.0	0.20	0.20	Ca:3	1170	127	1650	1430
203*	42.0	6.0	48.0	46.0	0.40	0.10	Ca:3	1170	136	700	1270
204	42.0	6.0	48.0	46.0	0.10	0.10	Ca:5	1170	107	3260	1930
205	42.0	6.0	48.0	46.0	0.20	0.10	Ca:5	1170	109	2590	1820
206	42.0	6.0	48.0	46.0	0.20	0.20	Ca:5	1170	112	1760	1760
207*	42.0	6.0	48.0	46.0	0.40	0.10	Ca:5	1170	119	740	1570
208(=65)	42.0	6.0	48.0	46.0	0.10	—	Ca:1 Sr:1	1170	146	2720	1430
209(=66)	42.0	6.0	48.0	46.0	0.10	—	Ca:1 Ba:1	1170	142	2550	1720
210(=67)	42.0	6.0	48.0	46.0	0.10	—	Ca:1 La:1	1170	129	2440	1880
211(=68)	42.0	6.0	48.0	46.0	0.10	—	Ba:2 La:2	1170	122	2220	2320
212	42.0	6.0	48.0	46.0	0.10	0.10	Ba:2 La:2	1170	132	1900	2290
213	42.0	6.0	48.0	46.0	0.30	0.10	Ba:2 La:2	1170	135	1060	1970
214*	42.0	6.0	48.0	46.0	0.40	0.10	Ba:2 La:2	1170	148	650	1860
215(=69)	42.0	6.0	48.0	46.0	0.10	—	Ba:3 La:2	1170	115	1780	2450
216(=70)*	42.0	6.0	48.0	46.0	0.10	—	Ba:4 La:2	1170	82	1700	3250

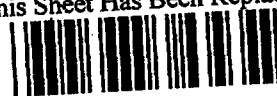
* Examples for comparison according to the prior art

Table 11

Sample No.	Composition						Type and quantity of element to replace Pb (mol %)	Firing Temp (°C)	Characteristic		
	X (%)	a (mol %)	b (mol %)	c (mol %)	Mg (% by weight)	Co (% by weight)	Ni (% by weight)		d ₃₁ (p C/N)	Q _m	C-TC (ppm/°C)
217	42.0	6.0	48.0	46.0	—	—	—	1170	128	2290	1810
218	42.0	6.0	48.0	46.0	0.10	—	—	1170	118	3280	1660
219	42.0	6.0	48.0	46.0	0.50	—	—	1170	126	1440	1550
220*	42.0	6.0	48.0	46.0	0.60	—	—	1170	141	700	1370
221	42.0	6.0	48.0	46.0	0.10	0.10	—	1170	123	2700	1730
222	42.0	6.0	48.0	46.0	0.40	0.10	—	1170	131	1490	1630
223	42.0	6.0	48.0	46.0	0.50	0.10	—	1170	121	760	1600
224	42.0	6.0	48.0	46.0	0.10	0.10	0.10	1170	128	2810	1640
225	42.0	6.0	48.0	46.0	0.30	0.10	0.10	1170	131	1120	1410
226*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	1170	143	650	1330
227*	42.0	6.0	48.0	46.0	0.10	—	—	1170	80	2590	2650

* Examples for comparison according to the prior art

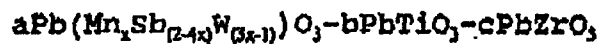
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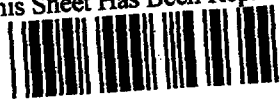
ABSTRACT OF THE DISCLOSURE

~~[There is provided a]~~ A piezoelectric ceramic composition is expressed by a general formula:



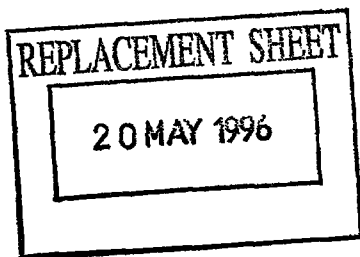
where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$ respectively (a, b, and c represent mol %, and $a + b + c = 100$). The composition has a large piezoelectric constant and a large mechanical factor of merit, is stable in temperature characteristics, and can be fired at low temperatures.

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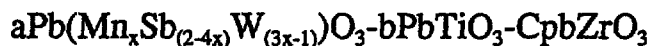


REPLACED SHEETS		SG
☐	Description	: paged to paged
☒	Claim(s)	: paged <u>13</u> to paged
☐	Drawing(s)	: paged to paged
☐	Abstract	: paged to paged

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What is claimed is :

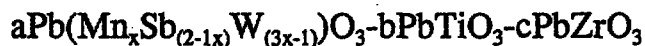
1. A piezoelectric ceramic composition expressed by a general formula :



where a, b, and c represent mol % and are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$, respectively, and $a + b + c = 100$.

2. A piezoelectric ceramic composition according to claim 1, further comprising at least one of magnesium, cobalt, and nickel in a ration of 0.50% or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO , NiO to the piezoelectric ceramic composition.

3. A piezoelectric ceramic composition expressed by a general formula :



where a, b, and c represent mol % and are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$, respectively, and $a + b + c = 100$, wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum.

4. A piezoelectric ceramic composition according to claim 3, wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum and further comprising at least one of magnesium, cobalt, and nickel in a ration of 0.50% or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO and NiO .

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- ☒ Description : paged to paged 23
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REPLACEMENT SHEET

Date 22 MAY 1996

1

PIEZOELECTRIC CERAMIC COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to piezoelectric ceramic compositions and, more particularly, to piezoelectric ceramic compositions preferably used in ultrasonic motors, ultrasonic vibrators, piezoelectric actuators, and the like.

2. Description of the Related Art

It is preferable that the piezoelectric materials (piezoelectric ceramic compositions) used in ultrasonic motors, ultrasonic vibrators, piezoelectric actuators, and the like have a large mechanical quality factor, less heat generation during the application of a high voltage, a large piezoelectric constant, and a large amplitude of vibration.

Further, it is important for piezoelectric materials for ultrasonic motors to have stable temperature characteristics to be able to provide stable speed of rotation and torque.

For conventional piezoelectric ceramic compositions, however, it is difficult to keep both the mechanical factor of merit and the piezoelectric constant sufficiently large, and the stability of the temperature characteristics is often not sufficient.

Piezoelectric ceramic compositions prepared to satisfy the above-described requirements as much as possible often have firing temperatures as high as 1200 to 1300 °C.

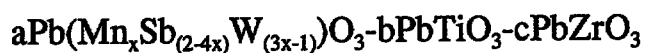
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SUMMARY OF THE INVENTION

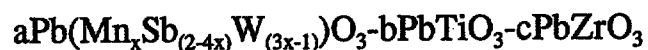
The preferred embodiments of the present invention solve the above-described problems, and provide a piezoelectric ceramic composition suitable for use as a material for ultrasonic motors, ultrasonic vibrators, and piezoelectric actuators, the piezoelectric ceramic composition having a large piezoelectric constant and a large mechanical factor of merit, stable temperature characteristics, and being adapted to be fired at low temperatures.

According to the preferred embodiments of the present invention, a piezoelectric ceramic composition has a general formula :



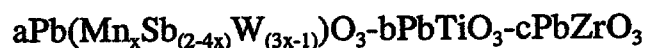
where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$).

According to another aspect of the preferred embodiments of the present invention, a piezoelectric ceramic composition comprises at least one of magnesium, cobalt, and nickel in a ratio of 50 % or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO , NiO , respectively, in a composition having a general formula :



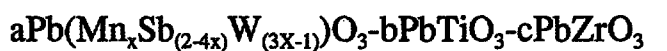
where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$).

According to another aspect of the preferred embodiments of the present invention, there is provided a piezoelectric ceramic composition having a general formula :



where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$) and wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum.

According to still another aspect of the preferred embodiments of the present invention, there is provided a piezoelectric ceramic composition expressed by a general formula :

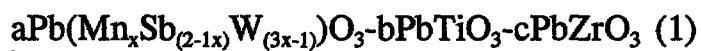


where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$), wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum and including at least one of magnesium, cobalt, and nickel in a ratio of 50 % or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO, and NiO.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The features of the present invention will now be more specifically described with reference to a preferred embodiments thereof.

Materials and additives PbO , TiO_2 , ZrO_2 , MnCO_3 , Sb_2O_3 , WO_3 are weighed to obtain the compositions as shown in Tables 1 through 4 and are subjected to wet mixing using a ball mill with a basic composition expressed by a general formula :



where $a + b + c = 100$, the ratios of x, a, b, and c being varied as shown in Tables 1 through 4. The values of magnesium, cobalt, and nickel in Tables 1 through 4 are the values of added magnesium, cobalt, and nickel compounds in terms of $\text{Mg}(\text{OH})_2$, CoO, and NiO, respectively.



The mixtures obtained as a result of the wet mixing are calcined for two hours at 850 to 950 °C, and the calcined materials are subjected to wet pulverization using a ball mill to obtain conditioned powders.

The conditioned powders are subjected to press molding after being combined with water or a binder such as polyvinyl alcohol and are fired for two hours at a temperature of 1100 to 1200 °C.

Next, the ceramics obtained as a result of the firing are ground to be in the form of a disc having a diameter of about 10 mm and a thickness of about 1 mm, and silver electrodes are applied on both and faces thereof. The ceramics are subjected to a polarization process for 60 minutes in an insulating oil at 80 °C using an electrical field of 3 to 4 KV to obtain piezoelectric ceramics.

Tables 1 through 4 show the measured characteristics of the piezoelectric ceramics obtained as described above.



The asterisked samples in Tables 1 through 4 are examples for comparison which are not in accordance with the preferred embodiments of the invention, and other samples are in accordance with the preferred embodiments of the present invention.

In tables 1 through 4, d31 represents a piezoelectric constant, Qm represents a mechanical factor of merit; and C-TC represents the temperature coefficient of an electrostatic capacity at -20 to 80 °C.

The piezoelectric characteristics were obtained through calculations of resonance frequencies and antiresonance frequencies measured by an impedance meter (in accordance with Japan Electronic Material Industrial Association Standard (EMAS-6100)). The measurement frequency for the temperature coefficient was 1 KHz.

In a piezoelectric ceramic composition according to the preferred embodiments of the present invention, the ratio of the third component of the basic composition and the ratio between the oxides, i.e., the value of a, b, and c, are defined as described above because ratios outside of this range will give undesirably small piezoelectric constants (d31) and mechanical factors of merit (Qm) and poor temperature coefficients (C-TC). The reasons for such a limitation will be described in the following paragraphs.

An examination of the characteristics of the piezoelectric ceramics (samples) having sample numbers 1 through 23 in Tables 1 and 2 indicates that for the samples (examples for comparison) in which the values of a, b, and c are not in accordance with the preferred embodiments of the present invention, at least one of the piezoelectric constant (d31) and the mechanical factor of merit (Qm) is



extremely small or the temperature coefficient (C-TC) is so large that the temperature characteristics deteriorate.

Referring to the value a, for example, for a sample whose value a is less than 2 mol %, such as the sample No. 7 on Table 1 (the value a is 1.0 mol % for the sample No. 7) the piezoelectric constant (d31) and mechanical factor of merit (Qm) are undesirable. As apparent from the sample No. 17 on Table 1, for a sample whose value a exceeds 10 mol % (the value a is 12.0 mol % for the sample No. 17), the temperature coefficient (C-TC) is undesirable and the piezoelectric constant (d31) and mechanical factor of merit (Qm) are poor.

It is therefore preferable that the value a in the above-described general formula (1) is in the range of about 2 to 10 mol %. In another preferred embodiment, the range for a is about 5 to 6 mol %.

Referring to the value b, for example, for a sample whose value b is less than 40 mol % such as the sample No. 18 on Table 1 (the value b is 38.0 mol % for the sample No. 18), the piezoelectric constant (d31) and mechanical factor of merit (Qm) are undesirable. Further, as apparent from the samples No. 22 and No. 23 on Table 2, a sample whose value b exceeds 52 mol % (the value b is 54.0 mol % and 58.0 mol % for the samples No. 22 and No. 23, respectively) has an undesirable piezoelectric constant (d31).

It is therefore preferable that the value b in the above-described general formula (1) is in the range of about 40 to 52 mol %. In another preferred embodiment, the range for b is about 44 to 50 mol %.

The value c in the above-described general formula (1) is a value which is automatically determined by the values



a and b because $a + b + c = 100$.

Although no limit is placed on the value x for a piezoelectric ceramic composition according to the preferred embodiments of the present invention, x is preferably in the range from about 35 % to about 48 % (from about 0.35 to 0.48) in order to obtain a practicable piezoelectric ceramic having good characteristics. For example, the piezoelectric ceramic having sample number 1 whose value x is less than 35 % (0.35) is susceptible to warpage and is therefore unpracticable. In another preferred embodiment, the range for x is about 36% to 42% (from about 0.36 to 0.42).

The samples No. 24 through No. 35 on Table 2 are piezoelectric ceramics which have been added with magnesium (magnesium compound) in varying amounts. Those samples indicate that although the addition of magnesium improves the mechanical factor of merit (Q_m), the mechanical factor of merit (Q_m) is conversely reduced significantly if the amount of magnesium added exceeds 50 % by weight in terms of $Mg(OH)_2$.

The samples No. 36 through No. 40 on Table 2 are piezoelectric ceramics which have been added with cobalt (cobalt compound) in varying amounts. Those samples indicate that the change in characteristics caused by the addition of cobalt has the same tendency as that caused by the addition of magnesium as described above.

The samples No. 41 through No. 45 on Table 2 are piezoelectric ceramics which have been added with nickel (nickel compound) in varying amounts. The change in characteristics caused by the addition of nickel also has the same tendency as that caused by the addition of magnesium as described above.

It is apparent from the samples No. 46 through No. 48 on Table 3 that the addition of two or more of the elements



magnesium (magnesium compound), cobalt (cobalt compound), and nickel (nickel compound) provides a piezoelectric ceramic having a large piezoelectric constant (d_{31}), a large mechanical factor of merit (Q_m), and good temperature characteristics. As apparent from the sample No. 49 on Table 3, however, the mechanical factor of merit (Q_m) tends to deteriorate significantly when the total amount of the added magnesium, cobalt, and nickel (the sum of the added values in terms of $Mg(OH)_2$, CoO , and NiO) exceeds 50 % by weight.

It is therefore necessary to adjust the amounts of the added magnesium, cobalt, and nickel in terms of $Mg(OH)_2$, CoO , and NiO , respectively, so that they total at 50 % or less by weight.

Further, Tables 5 and 6 show characteristics obtained by adding combinations of magnesium and cobalt, magnesium and nickel, cobalt and nickel, and magnesium, cobalt, and nickel. The values of magnesium, cobalt, and nickel shown in Tables 5 and 6 are the values of the added magnesium, cobalt, and nickel compounds in terms of $Mg(OH)_2$, CoO , and NiO , respectively. In Tables 5 and 6, the samples having asterisked sample numbers are examples for comparison which are not in accordance with the preferred embodiments of the present invention, and the remaining samples are in accordance with the preferred embodiments of the present invention.



For simplicity in comparison, the data for the samples No. 46 through No. 49 shown in Table 3 are duplicated in Tables 5 and 6.

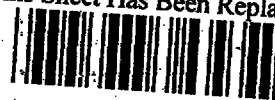
As apparent from Tables 5 and 6, piezoelectric ceramics having a large piezoelectric constant (d_{31}), a large mechanical factor of merit (Q_m), and good temperature characteristics can be obtained by adding magnesium, cobalt, and nickel in combinations wherein the amounts of those elements in terms of $Mg(OH)_2$, CoO , and NiO , respectively, are in ratios such that they total at 50 % or less by weight.

The samples No. 50 through No. 54 on Table 4 are samples wherein calcium is substituted for a part of lead. For the samples wherein the substituted amount is in accordance with the preferred embodiments of the present invention, the mechanical factor of merit (Q_m) is increased while the piezoelectric constant (d_{31}) and temperature coefficient ($C-TC$) are deteriorated when the substituted amount exceeds 5 mol % (sample No. 54). The substitution for lead (i.e., A-site) also provides another advantage in that the degree of sintering is improved.

It is further apparent from the samples No. 55 through No. 70 on Table 4 that the addition of magnesium, cobalt, and nickel to a system in which at least one of calcium, strontium, barium, and lanthanum is substituted for a part of lead, provides the same effect as that available in a system wherein lead is not substituted and that the piezoelectric constant (d_{31}) is improved when the added amounts in terms of $Mg(OH)_2$, CoO , and NiO total at 50 % or less by weight.

As apparent from the samples No. 57, 60, and 70, even in a system added with magnesium, cobalt, and nickel as described above, the piezoelectric constant (d_{31}) and temperature

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coefficient (C-TC) are deteriorated when the total amount of substitution with at least one of calcium, strontium, barium, and lanthanum exceeds 5 mol %.

It is therefore preferable that the amount of at least one of calcium, strontium, barium, and lanthanum substituted for a part of lead is 5 mol % or less.

However, the mechanical factor of merit (Q_m) tends to deteriorate even for a sample wherein lead (i.e., A-site) is substituted by 5 mol % or less when the amount of the added magnesium, cobalt, and nickel (the sum of the values of them in terms of $Mg(OH)_2$, CoO, and NiO, respectively) exceeds 0.50 % by weight (see sample No. 64).

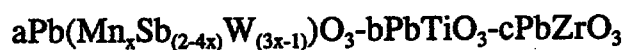
Tables 7 through 11 show characteristics obtained by various combinations of the addition of the additives magnesium, cobalt, and nickel and the elements for substitution calcium, strontium, barium, and lanthanum. In Tables 7 through 11, the values of magnesium, cobalt, and nickel are the values of the added magnesium, cobalt, and nickel compounds in terms of $Mg(OH)_2$, CoO, and NiO. Further, in Tables 7 through 11, the samples having asterisked sample numbers are examples for comparison which are not in accordance with the preferred embodiments of the present invention, and the remaining samples are preferred embodiments in accordance with the preferred embodiments of the present invention.



For simplicity in comparison, the data for the samples No. 50 through No. 70 shown in Table 4 as described above are duplicated in Tables 7 through 11.

As apparent from Tables 7 through 11, the combination of the addition of the additives magnesium, cobalt, and nickel and the substitution using the elements calcium, strontium, barium, and lanthanum provides a piezoelectric ceramic having a large piezoelectric constant (d31), a large mechanical factor of merit (Qm), and good temperature characteristics.

As described above, a piezoelectric ceramic composition according to the preferred embodiments of the present invention expressed by a general formula:

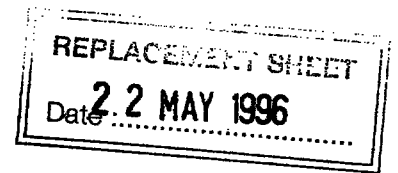


wherein the values (mol %) of a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively and at least one of magnesium, cobalt, and nickel is added as needed; and at least one of calcium, strontium, barium, and lanthanum is substituted for a part of lead, has a large piezoelectric constant and a large mechanical factor of merit, has stable temperature characteristics, and consistently provides large vibrations even under conditions wherein the temperature fluctuates.

In addition, since it can be fired at a temperature which is about 100 °C lower than that for conventional piezoelectric ceramic compositions, it is possible to obtain a piezoelectric ceramic having good reproducibility by suppressing the vaporization of the lead oxide.

Therefore, a piezoelectric ceramic composition according to the preferred embodiments of the present invention is advantageous especially as a piezoelectric material for ultrasonic motors, ultrasonic vibrators, piezoelectric actuators,





and the like and is suitable for a variety of industrial purposes.

While specific preferred embodiments have been described, it will be appreciated by those skilled in the art that various modifications, changes and additions can be made to the invention without departing from the spirit and scope thereof as set forth in the following claims.

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Date **22 MAY 1996**

Table 1

Sample No.	Composition						Firing Temp °C	Characteristics		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight	d ₃₁ p C/N	Q _m	C-TC ppm/°C
1	34.5	6.0	48.0	46.0	—	—	—	138	1850	2450
2	35.0	6.0	48.0	46.0	—	—	—	164	1870	1870
3	39.0	6.0	48.0	46.0	—	—	—	153	1880	1780
4	42.0	6.0	48.0	46.0	—	—	—	150	1840	1660
5	48.0	6.0	48.0	46.0	—	—	—	150	1980	1270
6	49.0	6.0	48.0	46.0	—	—	—	98	2200	1300
7*	42.0	1.0	44.0	55.0	—	—	—	45	800	1860
8	42.0	2.0	44.0	54.0	—	—	—	102	1400	2300
9	42.0	2.0	46.0	52.0	—	—	—	126	1420	1860
10	42.0	2.0	50.0	48.0	—	—	—	115	2170	1380
11	42.0	5.0	44.0	51.0	—	—	—	125	2350	2010
12	42.0	5.0	46.0	49.0	—	—	—	142	2350	1620
13	42.0	5.0	50.0	45.0	—	—	—	118	2490	1330
14	42.0	10.0	44.0	46.0	—	—	—	105	1960	3010
15	42.0	10.0	46.0	44.0	—	—	—	152	1370	2290
16	42.0	10.0	50.0	40.0	—	—	—	107	2240	1620
17*	42.0	12.0	44.0	44.0	—	—	—	52	650	3560
18*	36.0	5.0	38.0	57.0	—	—	—	48	3020	4530
19	36.0	5.0	40.0	55.0	—	—	—	100	2020	3720
20	36.0	5.0	46.0	49.0	—	—	—	142	1620	1920

* Examples for comparison according to the prior art

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22 MAY 1996

Date

Table 2

Sample No.	Composition						Firing Temp °C	Characteristics		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight	d ₃₁ p C/N	Qm	C-TC ppm°C
21	36.0	5.0	52.0	43.0	—	—	—	99	2560	1250
22*	36.0	5.0	54.0	41.0	—	—	—	63	2870	970
23*	36.0	5.0	58.0	37.0	—	—	—	35	4230	1320
24	42.0	6.0	48.0	46.0	0.10	—	—	138	3120	1520
25	42.0	6.0	48.0	46.0	0.15	—	—	150	2500	1420
26	42.0	6.0	46.0	48.0	0.20	—	—	102	2890	1990
27*	42.0	6.0	48.0	46.0	0.20	—	—	141	2420	1520
28	42.0	6.0	50.0	44.0	0.20	—	—	115	2890	1180
29	42.0	6.0	46.0	48.0	0.30	—	—	109	2920	1930
30	42.0	6.0	48.0	46.0	0.30	—	—	152	2330	1440
31	42.0	6.0	49.0	45.0	0.30	—	—	129	2780	1060
32	42.0	6.0	50.0	44.0	0.30	—	—	114	3000	920
33	42.0	6.0	46.0	48.0	0.50	—	—	125	1270	1830
34	42.0	6.0	48.0	46.0	0.50	—	—	148	1160	1420
35*	42.0	6.0	48.0	46.0	0.60	—	—	165	560	1260
36	42.0	6.0	46.0	48.0	—	0.20	—	125	2760	1820
37	42.0	6.0	48.0	46.0	—	0.20	—	156	2330	1430
38	42.0	6.0	50.0	44.0	—	0.20	—	118	2590	1110
39	42.0	6.0	48.0	46.0	—	0.50	—	162	1320	1320
40*	42.0	6.0	48.0	46.0	—	0.60	—	166	690	1210

* Examples for comparison according to the prior art

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Table 3

Sample No.	Composition							Firing Temp °C	Characteristics		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight		d ₃₁ p C/N	Q _m	C-TC ppm/°C
41	42.0	6.0	48.0	48.0	—	—	0.20	1150	127	2650	2050
42	42.0	6.0	48.0	46.0	—	—	0.20	1150	148	2210	1330
43	42.0	6.0	50.0	46.0	—	—	0.20	1150	124	1330	1070
44	42.0	6.0	48.0	46.0	—	—	0.50	1150	144	1170	920
45*	42.0	6.0	48.0	46.0	—	—	0.60	1150	155	730	960
46	42.0	5.0	49.0	46.0	0.20	0.10	—	1190	145	2250	1520
47	42.0	5.0	49.0	46.0	0.20	—	0.10	1190	138	2110	1380
48	42.0	5.0	49.0	46.0	0.40	0.10	—	1190	153	1200	1490
49*	42.0	5.0	49.0	46.0	0.50	0.10	—	1190	142	610	1470

* Examples for comparison according to the prior art

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Date 22 MAY 1996

Table 4

Sample No.	Composition						Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight		d ₃₁ p C/N	Qm	C-TC ppm/°C
50	42.0	6.0	48.0	46.0	—	—	—	1170	132	2320	1380
51	42.0	6.0	48.0	46.0	—	—	—	1170	126	2380	1510
52	42.0	6.0	48.0	46.0	—	—	—	1170	121	2470	1730
53	42.0	6.0	48.0	46.0	—	—	—	1170	102	2630	2130
54*	42.0	6.0	48.0	46.0	—	—	—	1170	63	2710	2640
55	42.0	6.0	48.0	46.0	—	—	0.20	1170	148	2430	1570
56	42.0	6.0	48.0	46.0	—	—	0.20	1170	125	2550	2060
57*	42.0	6.0	48.0	46.0	—	—	0.20	1170	69	2590	2560
58	42.0	6.0	48.0	46.0	—	—	0.20	1170	145	2320	1530
59	42.0	6.0	48.0	46.0	—	—	0.20	1170	120	2560	2070
60*	42.0	6.0	48.0	46.0	—	—	0.20	1170	72	2580	2570
61	42.0	6.0	48.0	46.0	—	0.10	—	1170	129	2120	1520
62	42.0	6.0	48.0	46.0	—	0.20	—	1170	134	2330	1410
63	42.0	6.0	48.0	46.0	—	0.50	—	1170	157	1510	1530
64*	42.0	6.0	48.0	46.0	—	0.60	—	1170	162	780	1580
65	42.0	6.0	48.0	46.0	0.10	—	—	1170	146	2720	1430
66	42.0	6.0	48.0	46.0	0.10	—	—	1170	142	2550	1720
67	42.0	6.0	48.0	46.0	0.10	—	—	1170	129	2440	1880
68	42.0	6.0	48.0	46.0	0.10	—	—	1170	122	2220	2320
69	42.0	6.0	48.0	46.0	0.10	—	—	1170	115	1790	2450
70*	42.0	6.0	48.0	46.0	0.10	—	—	1170	82	1700	3250

* Examples for comparison according to the prior art

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Date 22 MAY 1996

Table 5

Sample No.	Composition						Firing Temp °C	Characteristics		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight	d ₃₁ p C/N	Qm	C-TC ppm/°C
101	42.0	5.0	49.0	46.0	0.10	0.10	—	144	2330	1590
102	42.0	5.0	49.0	46.0	0.10	0.40	—	152	1160	1480
103*	42.0	5.0	49.0	46.0	0.10	0.50	—	164	410	1320
104(=46)	42.0	5.0	49.0	46.0	0.20	0.10	—	145	2250	1520
105	42.0	5.0	49.0	46.0	0.20	0.30	—	157	1260	1330
106*	42.0	5.0	49.0	46.0	0.20	0.40	—	163	660	1240
107(=48)	42.0	5.0	49.0	46.0	0.40	0.10	—	153	1200	1490
108*	42.0	5.0	49.0	46.0	0.40	0.20	—	159	480	1330
109(=49)*	42.0	5.0	49.0	46.0	0.50	0.10	—	142	610	1470
110	42.0	5.0	49.0	46.0	0.10	—	0.10	129	2010	1560
111	42.0	5.0	49.0	46.0	0.10	—	0.40	139	1110	1320
112*	42.0	5.0	49.0	46.0	0.10	—	0.50	152	420	1190
113(=47)	42.0	5.0	49.0	46.0	0.20	—	0.10	138	2110	1380
114	42.0	5.0	49.0	46.0	0.20	—	0.30	144	1020	1310
115*	42.0	5.0	49.0	46.0	0.20	—	0.40	151	390	1270
116	42.0	5.0	49.0	46.0	0.40	—	0.10	142	1070	1390
117*	42.0	5.0	49.0	46.0	0.40	—	0.20	162	520	1220
118*	42.0	5.0	49.0	46.0	0.50	—	0.10	164	550	1230
119	42.0	5.0	49.0	46.0	—	0.10	0.10	143	2550	1480
120	42.0	5.0	49.0	46.0	—	0.10	0.40	155	1230	1380

* Examples for comparison according to the prior art

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Table 6

Sample No.	Composition							Firing Temp °C	Characteristics		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight		ds ₁ p C/N	Qm	C-TC ppm/°C
121*	42.0	5.0	49.0	46.0	—	0.10	0.50	1190	167	440	1320
122	42.0	5.0	49.0	46.0	—	0.20	0.10	1190	151	2330	1410
123	42.0	5.0	49.0	46.0	—	0.20	0.30	1190	153	1160	1320
124*	42.0	5.0	49.0	46.0	—	0.20	0.40	1190	159	560	1310
125	42.0	5.0	49.0	46.0	—	0.40	0.10	1190	128	1200	1400
126*	42.0	5.0	49.0	46.0	—	0.40	0.20	1190	149	500	1220
127*	42.0	5.0	49.0	46.0	—	0.50	0.10	1190	157	480	1260
128	42.0	5.0	49.0	46.0	—	0.10	0.10	1190	150	2420	1500
129	42.0	5.0	49.0	46.0	0.10	0.10	0.10	1190	153	1810	1420
130	42.0	5.0	49.0	46.0	0.20	0.20	0.10	1190	157	1230	1370
131*	42.0	5.0	49.0	46.0	0.20	0.10	0.10	1190	168	520	1220
132	42.0	5.0	49.0	46.0	0.40	0.20	0.10	1190	154	1800	1390
133	42.0	5.0	49.0	46.0	0.10	0.20	0.20	1190	158	1330	1360
134*	42.0	5.0	49.0	46.0	0.10	0.40	0.10	1190	172	490	1110
135	42.0	5.0	49.0	46.0	0.10	0.10	0.20	1190	151	1880	1390
136	42.0	5.0	49.0	46.0	0.20	0.10	0.20	1190	152	1090	1320
137*	42.0	5.0	49.0	46.0	0.10	0.10	0.40	1190	154	480	1250

* Examples for comparison according to the prior art



Table 7

Sample No.	Composition						Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight			d ₃₁ p C/N	Qm	C-TC ppm/°C.
138(=50)	42.0	6.0	48.0	46.0	—	—	Ca:1	1170	132	2320	1380
139(=51)	42.0	6.0	48.0	46.0	—	—	Ca:2	1170	126	2380	1510
140(=52)	42.0	6.0	48.0	46.0	—	—	Ca:3	1170	121	2470	1730
141(=53)	42.0	6.0	48.0	46.0	—	—	Ca:5	1170	102	2630	2130
142(=54*)	42.0	6.0	48.0	46.0	—	—	Ca:6	1170	63	2710	2640
143	42.0	6.0	48.0	46.0	—	—	Sr:1	1170	142	1940	1360
144	42.0	6.0	48.0	46.0	—	—	Sr:5	1170	107	2430	2110
145*	42.0	6.0	48.0	46.0	—	—	Sr:6	1170	74	2600	2530
146	42.0	6.0	48.0	46.0	—	—	Ba:1	1170	138	1970	1400
147	42.0	6.0	48.0	46.0	—	—	Ba:5	1170	104	2540	2120
148*	42.0	6.0	48.0	46.0	—	—	Ba:6	1170	69	2720	2510
149	42.0	6.0	48.0	46.0	—	—	La:1	1170	136	2000	1370
150	42.0	6.0	48.0	46.0	—	—	La:5	1170	105	2510	2010
151*	42.0	6.0	48.0	46.0	—	—	La:6	1170	60	2790	2500
152	42.0	6.0	48.0	46.0	0.10	—	Ba:2	1170	121	3230	1260
153	42.0	6.0	48.0	46.0	0.50	—	Ca:1	1170	130	1460	1180
154*	42.0	6.0	48.0	46.0	0.60	—	Ca:1	1170	145	700	1050
155	42.0	6.0	48.0	46.0	—	0.10	Ca:1	1170	125	3080	1250
156	42.0	6.0	48.0	46.0	—	0.50	Ca:1	1170	143	1660	1100
157*	42.0	6.0	48.0	46.0	—	0.60	Ca:1	1170	146	870	1010

* Examples for comparison according to the prior art



Date **22 MAY 1996**

Table 8

Sample No.	Composition						Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight		d ₃₁ p C/N	Qm	C-TC ppm/°C
158	42.0	6.0	48.0	46.0	—	—	0.10	1170	121	3060	1040
159	42.0	6.0	48.0	46.0	—	—	0.50	1170	127	1480	860
160*	42.0	6.0	48.0	46.0	—	—	0.60	1170	136	790	900
161	42.0	6.0	48.0	46.0	0.10	—	—	1170	104	3760	1950
162	42.0	6.0	48.0	46.0	0.50	—	—	1170	111	1360	1820
163*	42.0	6.0	48.0	46.0	0.60	—	—	1170	122	800	1620
164	42.0	6.0	48.0	46.0	—	0.10	—	1170	107	3500	1930
165	42.0	6.0	48.0	46.0	—	0.50	—	1170	120	1590	1700
166*	42.0	6.0	48.0	46.0	—	0.60	—	1170	123	820	1550
167	42.0	6.0	48.0	46.0	—	—	0.10	1170	104	3600	1600
168	42.0	6.0	48.0	46.0	—	—	0.50	1170	108	1370	1180
169*	42.0	6.0	48.0	46.0	—	—	0.60	1170	115	740	1230
170*	42.0	6.0	48.0	46.0	0.10	—	—	1170	58	3700	2520
171(-55)	42.0	6.0	48.0	46.0	—	—	0.20	1170	148	2430	1570
172	42.0	6.0	48.0	46.0	—	—	0.50	1170	152	1330	1480
173*	42.0	6.0	48.0	46.0	—	—	0.60	1170	156	710	1460
174(=56)	42.0	6.0	48.0	46.0	—	—	0.20	1170	125	2550	2060
175	42.0	6.0	48.0	46.0	—	—	0.50	1170	128	1420	1870
176*	42.0	6.0	48.0	46.0	—	—	0.60	1170	132	730	1750
177(=57)*	42.0	6.0	48.0	46.0	—	—	0.20	1170	69	2590	2560

* Examples for comparison according to the prior art

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Date 22 MAY 1996

Table 9

Sample No.	Composition						Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight		da1 p C/N	Qm	C-TC ppm/°C
178(=61)	42.0	6.0	48.0	46.0	—	0.10	—	1170	129	2120	1520
179(=62)	42.0	6.0	48.0	46.0	—	0.20	—	1170	134	2330	1410
180(=63)	42.0	6.0	48.0	46.0	—	0.50	—	1170	157	1510	1530
181(=64)*	42.0	6.0	48.0	46.0	—	0.60	—	1170	162	780	1580
182(=58)	42.0	6.0	48.0	46.0	—	—	0.20	1170	145	2320	1530
183	42.0	6.0	48.0	46.0	—	—	0.50	1170	151	1280	1400
184*	42.0	6.0	48.0	46.0	—	—	0.60	1170	156	790	1380
185(=59)	42.0	6.0	48.0	46.0	—	—	0.20	1170	120	2560	2070
186	42.0	6.0	48.0	46.0	—	—	0.50	1170	132	1390	1850
187*	42.0	6.0	48.0	46.0	—	—	0.60	1170	136	770	1780
188(=60)*	42.0	6.0	48.0	46.0	—	—	0.20	1170	72	2580	2570
189	42.0	6.0	48.0	46.0	—	—	0.20	1170	145	2330	1630
190	42.0	6.0	48.0	46.0	—	—	0.50	1170	150	1280	1520
191*	42.0	6.0	48.0	46.0	—	—	0.60	1170	152	760	1440
192	42.0	6.0	48.0	46.0	—	—	0.20	1170	122	2470	2130
193	42.0	6.0	48.0	46.0	—	—	0.50	1170	131	1320	1770
194*	42.0	6.0	48.0	46.0	—	—	0.60	1170	139	700	1740
195*	42.0	6.0	48.0	46.0	—	—	0.20	1170	77	2620	2710
196	42.0	6.0	48.0	46.0	0.10	0.10	0.10	1170	132	2850	1250
197	42.0	6.0	48.0	46.0	0.20	0.10	0.10	1170	135	2280	1180

* Examples for comparison according to the prior art



Table 10

Sample No.	Composition							Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight			d ₃₁ p C/N	Qm	C-TC ppm/°C
198	42.0	6.0	48.0	46.0	0.20	0.20	0.10	Ca:1	1170	138	1550	1140
199*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	Ca:1	1170	148	660	1010
200	42.0	6.0	48.0	46.0	0.10	0.10	0.10	Ca:3	1170	121	3050	1560
201	42.0	6.0	48.0	46.0	0.20	0.10	0.10	Ca:3	1170	123	2430	1480
202	42.0	6.0	48.0	46.0	0.20	0.20	0.10	Ca:3	1170	127	1650	1430
203*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	Ca:3	1170	136	700	1270
204	42.0	6.0	48.0	46.0	0.10	0.10	0.10	Ca:5	1170	107	3260	1930
205	42.0	6.0	48.0	46.0	0.20	0.10	0.10	Ca:5	1170	109	2590	1820
206	42.0	6.0	48.0	46.0	0.20	0.20	0.10	Ca:5	1170	112	1760	1760
207*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	Ca:5	1170	119	740	1570
208(=65)	42.0	6.0	48.0	46.0	0.10	—	—	Ca:1 Sr:1	1170	146	2720	1430
209(=66)	42.0	6.0	48.0	46.0	0.10	—	—	Ca:1 Ba:1	1170	142	2550	1720
210(=67)	42.0	6.0	48.0	46.0	0.10	—	—	Ca:1 La:1	1170	129	2440	1880
211(=68)	42.0	6.0	48.0	46.0	0.10	—	—	Ba:2 La:2	1170	122	2220	2320
212	42.0	6.0	48.0	46.0	0.10	0.10	0.10	Ba:2 La:2	1170	132	1900	2290
213	42.0	6.0	48.0	46.0	0.30	0.10	0.10	Ba:2 La:2	1170	135	1060	1970
214*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	Ba:2 La:2	1170	148	650	1860
215(=69)	42.0	6.0	48.0	46.0	0.10	—	—	Ba:3 La:2	1170	115	1780	2450
216(=70)*	42.0	6.0	48.0	46.0	0.10	—	—	Ba:4 La:2	1170	82	1700	3250

* Examples for comparison according to the prior art



Table 11

Sample No.	Composition							Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight			d ₃₁ p C/N	Qm	C-TC ppm°C
217	42.0	6.0	48.0	46.0	—	—	—	Ca:1 Sr:1 Ba:1 La:1	1170	128	2290	1810
218	42.0	6.0	48.0	46.0	0.10	—	—	Ca:1 Sr:1 Ba:1 La:1	1170	118	3280	1660
219	42.0	6.0	48.0	46.0	0.50	—	—	Ca:1 Sr:1 Ba:1 La:1	1170	126	1440	1550
220*	42.0	6.0	48.0	46.0	0.60	—	—	Ca:1 Sr:1 Ba:1 La:1	1170	141	700	1370
221	42.0	6.0	48.0	46.0	0.10	0.10	—	Ca:1 Sr:1 Ba:1 La:1	1170	123	2700	1730
222	42.0	6.0	48.0	46.0	0.40	0.10	—	Ca:1 Sr:1 Ba:1 La:1	1170	131	1490	1630
223	42.0	6.0	48.0	46.0	0.50	0.10	—	Ca:1 Sr:1 Ba:1 La:1	1170	121	760	1600
224	42.0	6.0	48.0	46.0	0.10	0.10	0.10	Ca:1 Sr:1 Ba:1 La:1	1170	128	2810	1640
225	42.0	6.0	48.0	46.0	0.30	0.10	0.10	Ca:1 Sr:1 Ba:1 La:1	1170	131	1120	1410
226*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	Ca:1 Sr:1 Ba:1 La:1	1170	143	650	1330
227*	42.0	6.0	48.0	46.0	0.10	—	—	Ca:3 Sr:1 Ba:1 La:1	1170	80	2590	2650

* Examples for comparison according to the prior art

REPLACEMENT SHEET

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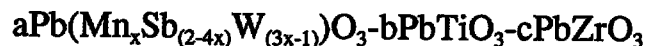
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What is claimed is :

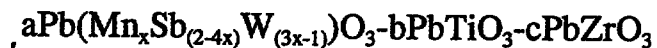
1. A piezoelectric ceramic composition expressed by a general formula :



where a, b, and c represent mol % and are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$, respectively, and $a + b + c = 100$.

2. A piezoelectric ceramic composition according to claim 1, further comprising at least one of magnesium, cobalt, and nickel in a ration of 0.50 % or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO , NiO to the piezoelectric ceramic composition.

3. A piezoelectric ceramic composition expressed by a general formula :



where a, b, and c represent mol % and are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$, respectively, and $a + b + c = 100$, wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum.

4. A piezoelectric ceramic composition according to claim 3, wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum and further comprising at least one of magnesium, cobalt, and nickel in a ration of 0.50% or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO and NiO .



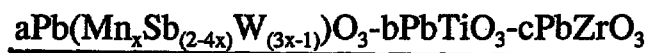
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ABSTRACT OF THE DISCLOSURE

PIEZOELECTRIC CERAMIC COMPOSITIONS

A piezoelectric ceramic composition is expressed by a general formula:



where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$ respectively (a, b, and c represent mol %, and $a + b + c = 100$). The composition has a large piezoelectric constant and a large mechanical factor of merit, is stable in temperature characteristics, and can be fired at low temperatures.

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PIEZOELECTRIC CERAMIC COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to piezoelectric ceramic compositions and, more particularly, to piezoelectric ceramic compositions preferably used in ultrasonic motors, ultrasonic vibrators, piezoelectric actuators, and the like.

2. Description of the Related Art

It is preferable that the piezoelectric materials (piezoelectric ceramic compositions) used in ultrasonic motors, ultrasonic vibrators, piezoelectric actuators, and the like have a large mechanical quality factor, less heat generation during the application of a high voltage, a large piezoelectric constant, and a large amplitude of vibration.

Further, it is important for piezoelectric materials for ultrasonic motors to have stable temperature characteristics to be able to provide stable speed of rotation and torque.

For conventional piezoelectric ceramic compositions, however, it is difficult to keep both the mechanical factor of merit and the piezoelectric constant sufficiently large, and the stability of the temperature characteristics is often not sufficient.

Piezoelectric ceramic compositions prepared to satisfy the above-described requirements as much as possible often have firing temperatures as high as 1200 to 1300 °C.

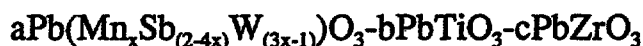
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SUMMARY OF THE INVENTION

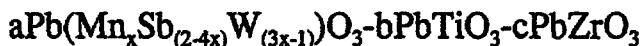
The preferred embodiments of the present invention solve the above-described problems, and provide a piezoelectric ceramic composition suitable for use as a material for ultrasonic motors, ultrasonic vibrators, and piezoelectric actuators, the piezoelectric ceramic composition having a large piezoelectric constant and a large mechanical factor of merit, stable temperature characteristics, and being adapted to be fired at low temperatures.

According to the preferred embodiments of the present invention, a piezoelectric ceramic composition has a general formula :



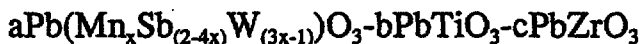
where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$).

According to another aspect of the preferred embodiments of the present invention, a piezoelectric ceramic composition comprises at least one of magnesium, cobalt, and nickel in a ratio of 50 % or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO , NiO , respectively, in a composition having a general formula :



where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$).

According to another aspect of the preferred embodiments of the present invention, there is provided a piezoelectric ceramic composition having a general formula :

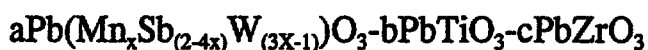


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where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$) and wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum.

According to still another aspect of the preferred embodiments of the present invention, there is provided a piezoelectric ceramic composition expressed by a general formula :

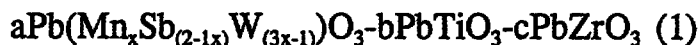


where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively (a, b, and c represent mol %, and $a + b + c = 100$), wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum and including at least one of magnesium, cobalt, and nickel in a ratio of 50 % or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO , and NiO .

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The features of the present invention will now be more specifically described with reference to a preferred embodiments thereof.

Materials and additives PbO , TiO_2 , ZrO_2 , MnCO_3 , Sb_2O_3 , WO_3 are weighed to obtain the compositions as shown in Tables 1 through 4 and are subjected to wet mixing using a ball mill with a basic composition expressed by a general formula :



where $a + b + c = 100$, the ratios of x, a, b, and c being varied as shown in Tables 1 through 4. The values of magnesium, cobalt, and nickel in Tables 1 through 4 are the values of added magnesium, cobalt, and nickel compounds in terms of $\text{Mg}(\text{OH})_2$, CoO , and NiO , respectively.

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The mixtures obtained as a result of the wet mixing are calcined for two hours at 850 to 950 °C, and the calcined materials are subjected to wet pulverization using a ball mill to obtain conditioned powders.

The conditioned powders are subjected to press molding after being combined with water or a binder such as polyvinyl alcohol and are fired for two hours at a temperature of 1100 to 1200 °C.

Next, the ceramics obtained as a result of the firing are ground to be in the form of a disc having a diameter of about 10 mm and a thickness of about 1 mm, and silver electrodes are applied on both and faces thereof. The ceramics are subjected to a polarization process for 60 minutes in an insulating oil at 80 °C using an electrical field of 3 to 4 KV to obtain piezoelectric ceramics.

Tables 1 through 4 show the measured characteristics of the piezoelectric ceramics obtained as described above.

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The asterisked samples in Tables 1 through 4 are examples for comparison which are not in accordance with the preferred embodiments of the invention, and other samples are in accordance with the preferred embodiments of the present invention.

In tables 1 through 4, d_{31} represents a piezoelectric constant, Q_m represents a mechanical factor of merit; and C-TC represents the temperature coefficient of an electrostatic capacity at -20 to 80 °C.

The piezoelectric characteristics were obtained through calculations of resonance frequencies and antiresonance frequencies measured by an impedance meter (in accordance with Japan Electronic Material Industrial Association Standard (EMAS-6100)). The measurement frequency for the temperature coefficient was 1 KHz.

In a piezoelectric ceramic composition according to the preferred embodiments of the present invention, the ratio of the third component of the basic composition and the ratio between the oxides, i.e., the value of a, b, and c, are defined as described above because ratios outside of this range will give undesirably small piezoelectric constants (d_{31}) and mechanical factors of merit (Q_m) and poor temperature coefficients (C-TC). The reasons for such a limitation will be described in the following paragraphs.

An examination of the characteristics of the piezoelectric ceramics (samples) having sample numbers 1 through 23 in Tables 1 and 2 indicates that for the samples (examples for comparison) in which the values of a, b, and c are not in accordance with the preferred embodiments of the present invention, at least one of the piezoelectric constant (d_{31}) and the mechanical factor of merit (Q_m) is

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extremely small or the temperature coefficient (C-TC) is so large that the temperature characteristics deteriorate.

Referring to the value a, for example, for a sample whose value a is less than 2 mol %, such as the sample No. 7 on Table 1 (the value a is 1.0 mol % for the sample No. 7) the piezoelectric constant (d31) and mechanical factor of merit (Qm) are undesirable. As apparent from the sample No. 17 on Table 1, for a sample whose value a exceeds 10 mol % (the value a is 12.0 mol % for the sample No. 17), the temperature coefficient (C-TC) is undesirable and the piezoelectric constant (d31) and mechanical factor of merit (Qm) are poor.

It is therefore preferable that the value a in the above-described general formula (1) is in the range of about 2 to 10 mol %. In another preferred embodiment, the range for a is about 5 to 6 mol %.

Referring to the value b, for example, for a sample whose value b is less than 40 mol % such as the sample No. 18 on Table 1 (the value b is 38.0 mol % for the sample No. 18), the piezoelectric constant (d31) and mechanical factor of merit (Qm) are undesirable. Further, as apparent from the samples No. 22 and No. 23 on Table 2, a sample whose value b exceeds 52 mol % (the value b is 54.0 mol % and 58.0 mol % for the samples No. 22 and No. 23, respectively) has an undesirable piezoelectric constant (d31).

It is therefore preferable that the value b in the above-described general formula (1) is in the range of about 40 to 52 mol %. In another preferred embodiment, the range for b is about 44 to 50 mol %.

The value c in the above-described general formula (1) is a value which is automatically determined by the values

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a and b because $a + b + c = 100$.

Although no limit is placed on the value x for a piezoelectric ceramic composition according to the preferred embodiments of the present invention, x is preferably in the range from about 35 % to about 48 % (from about 0.35 to 0.48) in order to obtain a practicable piezoelectric ceramic having good characteristics. For example, the piezoelectric ceramic having sample number 1 whose value x is less than 35 % (0.35) is susceptible to warpage and is therefore unpracticable. In another preferred embodiment, the range for x is about 36% to 42% (from about 0.36 to 0.42).

The samples No. 24 through No. 35 on Table 2 are piezoelectric ceramics which have been added with magnesium (magnesium compound) in varying amounts. Those samples indicate that although the addition of magnesium improves the mechanical factor of merit (Q_m), the mechanical factor of merit (Q_m) is conversely reduced significantly if the amount of magnesium added exceeds 50 % by weight in terms of $Mg(OH)_2$.

The samples No. 36 through No. 40 on Table 2 are piezoelectric ceramics which have been added with cobalt (cobalt compound) in varying amounts. Those samples indicate that the change in characteristics caused by the addition of cobalt has the same tendency as that caused by the addition of magnesium as described above.

The samples No. 41 through No. 45 on Table 2 are piezoelectric ceramics which have been added with nickel (nickel compound) in varying amounts. The change in characteristics caused by the addition of nickel also has the same tendency as that caused by the addition of magnesium as described above.

It is apparent from the samples No. 46 through No. 48 on Table 3 that the addition of two or more of the elements

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magnesium (magnesium compound), cobalt (cobalt compound), and nickel (nickel compound) provides a piezoelectric ceramic having a large piezoelectric constant (d_{31}), a large mechanical factor of merit (Q_m), and good temperature characteristics. As apparent from the sample No. 49 on Table 3, however, the mechanical factor of merit (Q_m) tends to deteriorate significantly when the total amount of the added magnesium, cobalt, and nickel (the sum of the added values in terms of $Mg(OH)_2$, CoO , and NiO) exceeds 50 % by weight.

It is therefore necessary to adjust the amounts of the added magnesium, cobalt, and nickel in terms of $Mg(OH)_2$, CoO , and NiO , respectively, so that they total at 50 % or less by weight.

Further, Tables 5 and 6 show characteristics obtained by adding combinations of magnesium and cobalt, magnesium and nickel, cobalt and nickel, and magnesium, cobalt, and nickel. The values of magnesium, cobalt, and nickel shown in Tables 5 and 6 are the values of the added magnesium, cobalt, and nickel compounds in terms of $Mg(OH)_2$, CoO , and NiO , respectively. In Tables 5 and 6, the samples having asterisked sample numbers are examples for comparison which are not in accordance with the preferred embodiments of the present invention, and the remaining samples are in accordance with the preferred embodiments of the present invention.

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For simplicity in comparison, the data for the samples No. 46 through No. 49 shown in Table 3 are duplicated in Tables 5 and 6.

As apparent from Tables 5 and 6, piezoelectric ceramics having a large piezoelectric constant (d_{31}), a large mechanical factor of merit (Q_m), and good temperature characteristics can be obtained by adding magnesium, cobalt, and nickel in combinations wherein the amounts of those elements in terms of $Mg(OH)_2$, CoO , and NiO , respectively, are in ratios such that they total at 50 % or less by weight.

The samples No. 50 through No. 54 on Table 4 are samples wherein calcium is substituted for a part of lead. For the samples wherein the substituted amount is in accordance with the preferred embodiments of the present invention, the mechanical factor of merit (Q_m) is increased while the piezoelectric constant (d_{31}) and temperature coefficient ($C-TC$) are deteriorated when the substituted amount exceeds 5 mol % (sample No. 54). The substitution for lead (i.e., A-site) also provides another advantage in that the degree of sintering is improved.

It is further apparent from the samples No. 55 through No. 70 on Table 4 that the addition of magnesium, cobalt, and nickel to a system in which at least one of calcium, strontium, barium, and lanthanum is substituted for a part of lead, provides the same effect as that available in a system wherein lead is not substituted and that the piezoelectric constant (d_{31}) is improved when the added amounts in terms of $Mg(OH)_2$, CoO , and NiO total at 50 % or less by weight.

As apparent from the samples No. 57, 60, and 70, even in a system added with magnesium, cobalt, and nickel as described above, the piezoelectric constant (d_{31}) and temperature

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coefficient (C-TC) are deteriorated when the total amount of substitution with at least one of calcium, strontium, barium, and lanthanum exceeds 5 mol %.

It is therefore preferable that the amount of at least one of calcium, strontium, barium, and lanthanum substituted for a part of lead is 5 mol % or less.

However, the mechanical factor of merit (Q_m) tends to deteriorate even for a sample wherein lead (i.e., A-site) is substituted by 5 mol % or less when the amount of the added magnesium, cobalt, and nickel (the sum of the values of them in terms of $Mg(OH)_2$, CoO, and NiO, respectively) exceeds 0.50 % by weight (see sample No. 64).

Tables 7 through 11 show characteristics obtained by various combinations of the addition of the additives magnesium, cobalt, and nickel and the elements for substitution calcium, strontium, barium, and lanthanum. In Tables 7 through 11, the values of magnesium, cobalt, and nickel are the values of the added magnesium, cobalt, and nickel compounds in terms of $Mg(OH)_2$, CoO, and NiO. Further, in Tables 7 through 11, the samples having asterisked sample numbers are examples for comparison which are not in accordance with the preferred embodiments of the present invention, and the remaining samples are preferred embodiments in accordance with the preferred embodiments of the present invention.

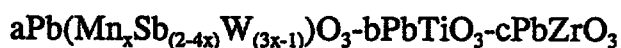
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For simplicity in comparison, the data for the samples No. 50 through No. 70 shown in Table 4 as described above are duplicated in Tables 7 through 11.

As apparent from Tables 7 through 11, the combination of the addition of the additives magnesium, cobalt, and nickel and the substitution using the elements calcium, strontium, barium, and lanthanum provides a piezoelectric ceramic having a large piezoelectric constant (d_{31}), a large mechanical factor of merit (Q_m), and good temperature characteristics.

As described above, a piezoelectric ceramic composition according to the preferred embodiments of the present invention expressed by a general formula:



wherein the values (mol %) of a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, respectively and at least one of magnesium, cobalt, and nickel is added as needed; and at least one of calcium, strontium, barium, and lanthanum is substituted for a part of lead, has a large piezoelectric constant and a large mechanical factor of merit, has stable temperature characteristics, and consistently provides large vibrations even under conditions wherein the temperature fluctuates.

In addition, since it can be fired at a temperature which is about 100 °C lower than that for conventional piezoelectric ceramic compositions, it is possible to obtain a piezoelectric ceramic having good reproducibility by suppressing the vaporization of the lead oxide.

Therefore, a piezoelectric ceramic composition according to the preferred embodiments of the present invention is advantageous especially as a piezoelectric material for ultrasonic motors, ultrasonic vibrators, piezoelectric actuators,

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and the like and is suitable for a variety of industrial purposes.

While specific preferred embodiments have been described, it will be appreciated by those skilled in the art that various modifications, changes and additions can be made to the invention without departing from the spirit and scope thereof as set forth in the following claims.

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Table 1

Sample No.	Composition						Firing Temp °C	Characteristics		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight	d ₃₁ p C/N	Q _m	C-TC ppm/°C
1	34.5	6.0	48.0	46.0	—	—	—	1150	138	1850
2	35.0	6.0	48.0	46.0	—	—	—	1150	164	1870
3	39.0	6.0	48.0	46.0	—	—	—	1150	153	1880
4	42.0	6.0	48.0	46.0	—	—	—	1150	150	1840
5	48.0	6.0	48.0	46.0	—	—	—	1150	150	1980
6	49.0	6.0	48.0	46.0	—	—	—	1150	98	2200
7*	42.0	1.0	44.0	55.0	—	—	—	1150	45	800
8	42.0	2.0	44.0	54.0	—	—	—	1150	102	1400
9	42.0	2.0	46.0	52.0	—	—	—	1150	126	1420
10	42.0	2.0	50.0	48.0	—	—	—	1150	115	2170
11	42.0	5.0	44.0	51.0	—	—	—	1150	125	2350
12	42.0	5.0	46.0	49.0	—	—	—	1150	142	2350
13	42.0	5.0	50.0	45.0	—	—	—	1150	118	2490
14	42.0	10.0	44.0	46.0	—	—	—	1150	105	1960
15	42.0	10.0	46.0	44.0	—	—	—	1150	152	1370
16	42.0	10.0	50.0	40.0	—	—	—	1150	107	2240
17*	42.0	12.0	44.0	44.0	—	—	—	1150	52	650
18*	36.0	5.0	38.0	57.0	—	—	—	1150	48	3020
19	36.0	5.0	40.0	55.0	—	—	—	1150	100	2020
20	36.0	5.0	46.0	49.0	—	—	—	1150	142	1620

* Examples for comparison according to the prior art

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Table 2

Sample No.	Composition						Firing Temp °C	Characteristics		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight	d ₃₁ p C/N	Qm	C-TC ppm/°C
21	36.0	5.0	52.0	43.0	—	—	—	99	2560	1250
22*	36.0	5.0	54.0	41.0	—	—	—	63	2870	970
23*	36.0	5.0	58.0	37.0	—	—	—	35	4230	1320
24	42.0	6.0	48.0	46.0	0.10	—	—	138	3120	1520
25	42.0	6.0	48.0	46.0	0.15	—	—	150	2500	1420
26	42.0	6.0	46.0	48.0	0.20	—	—	102	2890	1990
27*	42.0	6.0	48.0	46.0	0.20	—	—	141	2420	1520
28	42.0	6.0	50.0	44.0	0.20	—	—	115	2890	1180
29	42.0	6.0	46.0	48.0	0.30	—	—	109	2920	1930
30	42.0	6.0	48.0	46.0	0.30	—	—	152	2330	1440
31	42.0	6.0	49.0	45.0	0.30	—	—	129	2780	1060
32	42.0	6.0	50.0	44.0	0.30	—	—	114	3000	920
33	42.0	6.0	46.0	48.0	0.50	—	—	125	1270	1830
34	42.0	6.0	48.0	46.0	0.50	—	—	148	1160	1420
35*	42.0	6.0	48.0	46.0	0.60	—	—	165	560	1260
36	42.0	6.0	46.0	48.0	—	0.20	—	125	2760	1820
37	42.0	6.0	48.0	46.0	—	0.20	—	156	2330	1430
38	42.0	6.0	50.0	44.0	—	0.20	—	118	2590	1110
39	42.0	6.0	48.0	46.0	—	0.50	—	162	1320	1320
40*	42.0	6.0	48.0	46.0	—	0.60	—	166	690	1210

* Examples for comparison according to the prior art

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Table 3

Sample No.	Composition						Firing Temp °C	Characteristics		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight	d ₃₁ p C/N	Q _m	C-TC ppm/°C
41	42.0	6.0	48.0	48.0	—	—	0.20	127	2650	2050
42	42.0	6.0	48.0	46.0	—	—	0.20	148	2210	1330
43	42.0	6.0	50.0	46.0	—	—	0.20	124	1330	1070
44	42.0	6.0	48.0	46.0	—	—	0.50	144	1170	920
45*	42.0	6.0	48.0	46.0	—	—	0.60	155	730	960
46	42.0	5.0	49.0	46.0	0.20	0.10	—	145	2250	1520
47	42.0	5.0	49.0	46.0	0.20	—	0.10	138	2110	1380
48	42.0	5.0	49.0	46.0	0.40	0.10	—	153	1200	1490
49*	42.0	5.0	49.0	46.0	0.50	0.10	—	142	610	1470

* Examples for comparison according to the prior art

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Table 4

Sample No.	Composition						Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight		d ₃₁ p C/N	Qm	C-TC ppm/°C
50	42.0	6.0	48.0	46.0	—	—	—	1170	132	2320	1380
51	42.0	6.0	48.0	46.0	—	—	—	1170	126	2380	1510
52	42.0	6.0	48.0	46.0	—	—	—	1170	121	2470	1730
53	42.0	6.0	48.0	46.0	—	—	—	1170	102	2630	2130
54*	42.0	6.0	48.0	46.0	—	—	—	1170	63	2710	2640
55	42.0	6.0	48.0	46.0	—	—	0.20	1170	148	2430	1570
56	42.0	6.0	48.0	46.0	—	—	0.20	1170	125	2550	2060
57*	42.0	6.0	48.0	46.0	—	—	0.20	1170	69	2590	2560
58	42.0	6.0	48.0	46.0	—	—	0.20	1170	145	2320	1530
59	42.0	6.0	48.0	46.0	—	—	0.20	1170	120	2560	2070
60*	42.0	6.0	48.0	46.0	—	—	0.20	1170	72	2580	2570
61	42.0	6.0	48.0	46.0	—	0.10	—	1170	129	2120	1520
62	42.0	6.0	48.0	46.0	—	0.20	—	1170	134	2330	1410
63	42.0	6.0	48.0	46.0	—	0.50	—	1170	157	1510	1530
64*	42.0	6.0	48.0	46.0	—	0.60	—	1170	162	780	1580
65	42.0	6.0	48.0	46.0	0.10	—	—	1170	146	2720	1430
66	42.0	6.0	48.0	46.0	0.10	—	—	1170	142	2550	1720
67	42.0	6.0	48.0	46.0	0.10	—	—	1170	129	2440	1880
68	42.0	6.0	48.0	46.0	0.10	—	—	1170	122	2220	2320
69	42.0	6.0	48.0	46.0	0.10	—	—	1170	115	1780	2450
70*	42.0	6.0	48.0	46.0	0.10	—	—	1170	82	1700	3250

* Examples for comparison according to the prior art

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Table 5

Sample No.	Composition						Firing Temp °C	Characteristics		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight		d ₃₁ p C/N	Qm	C-TC ppm/°C
101	42.0	5.0	49.0	46.0	0.10	0.10	1190	144	2330	1590
102	42.0	5.0	49.0	46.0	0.10	0.40	1190	152	1160	1480
103*	42.0	5.0	49.0	46.0	0.10	0.50	1190	164	410	1320
104(=46)	42.0	5.0	49.0	46.0	0.20	0.10	1190	145	2250	1520
105	42.0	5.0	49.0	46.0	0.20	0.30	1190	157	1260	1330
106*	42.0	5.0	49.0	46.0	0.20	0.40	1190	163	660	1240
107(=48)	42.0	5.0	49.0	46.0	0.40	0.10	1190	153	1200	1490
108*	42.0	5.0	49.0	46.0	0.40	0.20	1190	159	480	1330
109(=49)*	42.0	5.0	49.0	46.0	0.50	0.10	1190	142	610	1470
110	42.0	5.0	49.0	46.0	0.10	—	1190	129	2010	1560
111	42.0	5.0	49.0	46.0	0.10	—	1190	139	1110	1320
112*	42.0	5.0	49.0	46.0	0.10	—	1190	152	420	1190
113(=47)	42.0	5.0	49.0	46.0	0.20	—	1190	138	2110	1380
114	42.0	5.0	49.0	46.0	0.20	—	1190	144	1020	1310
115*	42.0	5.0	49.0	46.0	0.20	—	1190	151	390	1270
116	42.0	5.0	49.0	46.0	0.40	—	1190	142	1070	1390
117*	42.0	5.0	49.0	46.0	0.40	—	1190	162	520	1220
118*	42.0	5.0	49.0	46.0	0.50	—	1190	164	550	1230
119	42.0	5.0	49.0	46.0	—	0.10	1190	143	2550	1480
120	42.0	5.0	49.0	46.0	—	0.10	1190	155	1230	1380

* Examples for comparison according to the prior art

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Table 6

Sample No.	Composition						Firing Temp °C	Characteristics		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight		d ₃₁ p C/N	Q _m	C-TC ppm/°C
121*	42.0	5.0	49.0	46.0	—	0.10	1190	167	440	1320
122	42.0	5.0	49.0	46.0	—	0.20	1190	151	2330	1410
123	42.0	5.0	49.0	46.0	—	0.20	1190	153	1160	1320
124*	42.0	5.0	49.0	46.0	—	0.20	1190	159	560	1310
125	42.0	5.0	49.0	46.0	—	0.40	1190	128	1200	1400
126*	42.0	5.0	49.0	46.0	—	0.40	1190	149	500	1220
127*	42.0	5.0	49.0	46.0	—	0.50	1190	157	480	1260
128	42.0	5.0	49.0	46.0	—	0.10	1190	150	2420	1500
129	42.0	5.0	49.0	46.0	0.10	0.10	1190	153	1810	1420
130	42.0	5.0	49.0	46.0	0.20	0.20	1190	157	1230	1370
131*	42.0	5.0	49.0	46.0	0.20	0.10	1190	168	520	1220
132	42.0	5.0	49.0	46.0	0.40	0.20	1190	154	1800	1390
133	42.0	5.0	49.0	46.0	0.10	0.20	1190	158	1330	1360
134*	42.0	5.0	49.0	46.0	0.10	0.40	1190	172	490	1110
135	42.0	5.0	49.0	46.0	0.10	0.10	1190	151	1880	1390
136	42.0	5.0	49.0	46.0	0.20	0.10	1190	152	1090	1320
137*	42.0	5.0	49.0	46.0	0.10	0.10	1190	154	480	1250

* Examples for comparison according to the prior art

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Table 7

Sample No.	Composition						Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight		d ₃₁ p C/N	Qm	C-TC ppm/°C.
138(=50)	42.0	6.0	48.0	46.0	—	—	—	1170	132	2320	1380
139(=51)	42.0	6.0	48.0	46.0	—	—	—	1170	126	2380	1510
140(=52)	42.0	6.0	48.0	46.0	—	—	—	1170	121	2470	1730
141(=53)	42.0	6.0	48.0	46.0	—	—	—	1170	102	2630	2130
142(=54*)	42.0	6.0	48.0	46.0	—	—	—	1170	63	2710	2640
143	42.0	6.0	48.0	46.0	—	—	—	1170	142	1940	1360
144	42.0	6.0	48.0	46.0	—	—	—	1170	107	2430	2110
145*	42.0	6.0	48.0	46.0	—	—	—	1170	74	2600	2530
146	42.0	6.0	48.0	46.0	—	—	—	1170	138	1970	1400
147	42.0	6.0	48.0	46.0	—	—	—	1170	104	2540	2120
148*	42.0	6.0	48.0	46.0	—	—	—	1170	69	2720	2510
149	42.0	6.0	48.0	46.0	—	—	—	1170	136	2000	1370
150	42.0	6.0	48.0	46.0	—	—	—	1170	105	2510	2010
151*	42.0	6.0	48.0	46.0	—	—	—	1170	60	2790	2500
152	42.0	6.0	48.0	46.0	0.10	—	—	1170	121	3230	1260
153	42.0	6.0	48.0	46.0	0.50	—	—	1170	130	1460	1180
154*	42.0	6.0	48.0	46.0	0.60	—	—	1170	145	700	1050
155	42.0	6.0	48.0	46.0	—	0.10	—	1170	125	3080	1250
156	42.0	6.0	48.0	46.0	—	0.50	—	1170	143	1660	1100
157*	42.0	6.0	48.0	46.0	—	0.60	—	1170	146	870	1010

* Examples for comparison according to the prior art

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Table 8

Sample No.	Composition						Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight		d ₃₁ pC/N	Q _m	C-TC ppm/°C
158	42.0	6.0	48.0	46.0	—	—	0.10	1170	121	3060	1040
159	42.0	6.0	48.0	46.0	—	—	0.50	1170	127	1480	860
160*	42.0	6.0	48.0	46.0	—	—	0.60	1170	136	790	900
161	42.0	6.0	48.0	46.0	0.10	—	—	1170	104	3760	1950
162	42.0	6.0	48.0	46.0	0.50	—	—	1170	111	1360	1820
163*	42.0	6.0	48.0	46.0	0.60	—	—	1170	122	800	1620
164	42.0	6.0	48.0	46.0	—	0.10	—	1170	107	3500	1930
165	42.0	6.0	48.0	46.0	—	0.50	—	1170	120	1590	1700
166*	42.0	6.0	48.0	46.0	—	0.60	—	1170	123	820	1550
167	42.0	6.0	48.0	46.0	—	—	0.10	1170	104	3600	1600
168	42.0	6.0	48.0	46.0	—	—	0.50	1170	108	1370	1180
169*	42.0	6.0	48.0	46.0	—	—	0.60	1170	115	740	1230
170*	42.0	6.0	48.0	46.0	0.10	—	—	1170	58	3700	2520
171(=55)	42.0	6.0	48.0	46.0	—	—	0.20	1170	148	2430	1570
172	42.0	6.0	48.0	46.0	—	—	0.50	1170	152	1330	1480
173*	42.0	6.0	48.0	46.0	—	—	0.60	1170	156	710	1460
174(=56)	42.0	6.0	48.0	46.0	—	—	0.20	1170	125	2550	2060
175	42.0	6.0	48.0	46.0	—	—	0.50	1170	128	1420	1870
176*	42.0	6.0	48.0	46.0	—	—	0.60	1170	132	730	1750
177(=57)*	42.0	6.0	48.0	46.0	—	—	0.20	1170	69	2590	2560

* Examples for comparison according to the prior art

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Table 9

Sample No.	Composition						Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight		d ₃₁ p C/N	Q _m	C-TC ppm/°C
178(=61)	42.0	6.0	48.0	46.0	—	0.10	—	1170	129	2120	1520
179(=62)	42.0	6.0	48.0	46.0	—	0.20	—	1170	134	2330	1410
180(=63)	42.0	6.0	48.0	46.0	—	0.50	—	1170	157	1510	1530
181(=64)*	42.0	6.0	48.0	46.0	—	0.60	—	1170	162	780	1580
182(=58)	42.0	6.0	48.0	46.0	—	—	0.20	1170	145	2320	1530
183	42.0	6.0	48.0	46.0	—	—	0.50	1170	151	1280	1400
184*	42.0	6.0	48.0	46.0	—	—	0.60	1170	156	790	1380
185(=59)	42.0	6.0	48.0	46.0	—	—	0.20	1170	120	2560	2070
186	42.0	6.0	48.0	46.0	—	—	0.50	1170	132	1390	1850
187*	42.0	6.0	48.0	46.0	—	—	0.60	1170	136	770	1780
188(=60)*	42.0	6.0	48.0	46.0	—	—	0.20	1170	72	2580	2570
189	42.0	6.0	48.0	46.0	—	—	0.20	1170	145	2330	1630
190	42.0	6.0	48.0	46.0	—	—	0.50	1170	150	1280	1520
191*	42.0	6.0	48.0	46.0	—	—	0.60	1170	152	760	1440
192	42.0	6.0	48.0	46.0	—	—	0.20	1170	122	2470	2130
193	42.0	6.0	48.0	46.0	—	—	0.50	1170	131	1320	1770
194*	42.0	6.0	48.0	46.0	—	—	0.60	1170	139	700	1740
195*	42.0	6.0	48.0	46.0	—	—	0.20	1170	77	2620	2710
196	42.0	6.0	48.0	46.0	0.10	0.10	0.10	1170	132	2850	1250
197	42.0	6.0	48.0	46.0	0.20	0.10	0.10	1170	135	2280	1180

* Examples for comparison according to the prior art

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Table 10

Sample No.	Composition							Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight			d ₃₁ p C/N	Qm	C-TC ppm/°C
198	42.0	6.0	48.0	46.0	0.20	0.20	0.10	Ca:1	1170	138	1550	1140
199*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	Ca:1	1170	148	660	1010
200	42.0	6.0	48.0	46.0	0.10	0.10	0.10	Ca:3	1170	121	3050	1560
201	42.0	6.0	48.0	46.0	0.20	0.10	0.10	Ca:3	1170	123	2430	1480
202	42.0	6.0	48.0	46.0	0.20	0.10	0.10	Ca:3	1170	127	1650	1430
203*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	Ca:3	1170	136	700	1270
204	42.0	6.0	48.0	46.0	0.10	0.10	0.10	Ca:5	1170	107	3260	1930
205	42.0	6.0	48.0	46.0	0.20	0.10	0.10	Ca:5	1170	109	2590	1820
206	42.0	6.0	48.0	46.0	0.20	0.20	0.10	Ca:5	1170	112	1760	1760
207*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	Ca:5	1170	119	740	1570
208(=65)	42.0	6.0	48.0	46.0	0.10	—	—	Ca:1 Sr:1	1170	146	2720	1430
209(=66)	42.0	6.0	48.0	46.0	0.10	—	—	Ca:1 Ba:1	1170	142	2550	1720
210(=67)	42.0	6.0	48.0	46.0	0.10	—	—	Ca:1 La:1	1170	129	2440	1880
211(=68)	42.0	6.0	48.0	46.0	0.10	—	—	Ba:2 La:2	1170	122	2220	2320
212	42.0	6.0	48.0	46.0	0.10	0.10	0.10	Ba:2 La:2	1170	132	1900	2290
213	42.0	6.0	48.0	46.0	0.30	0.10	0.10	Ba:2 La:2	1170	135	1060	1970
214*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	Ba:2 La:2	1170	148	650	1860
215(=69)	42.0	6.0	48.0	46.0	0.10	—	—	Ba:3 La:2	1170	115	1780	2450
216(=70)*	42.0	6.0	48.0	46.0	0.10	—	—	Ba:4 La:2	1170	82	1700	3250

* Examples for comparison according to the prior art

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Date: 14 JUN 1996

Table 11

Sample No.	Composition							Type and quantity of element to replace Pb mol %	Firing Temp °C	Characteristic		
	X %	a mol %	b mol %	c mol %	Mg % by weight	Co % by weight	Ni % by weight			d ₃₁ p C/N	Qm	C-TC ppm/°C
217	42.0	6.0	48.0	46.0	—	—	—	Ca:1 Sr:1 Ba:1 La:1	1170	128	2290	1810
218	42.0	6.0	48.0	46.0	0.10	—	—	Ca:1 Sr:1 Ba:1 La:1	1170	118	3280	1660
219	42.0	6.0	48.0	46.0	0.50	—	—	Ca:1 Sr:1 Ba:1 La:1	1170	126	1440	1550
220*	42.0	6.0	48.0	46.0	0.60	—	—	Ca:1 Sr:1 Ba:1 La:1	1170	141	700	1370
221	42.0	6.0	48.0	46.0	0.10	0.10	—	Ca:1 Sr:1 Ba:1 La:1	1170	123	2700	1730
222	42.0	6.0	48.0	46.0	0.40	0.10	—	Ca:1 Sr:1 Ba:1 La:1	1170	131	1490	1630
223	42.0	6.0	48.0	46.0	0.50	0.10	—	Ca:1 Sr:1 Ba:1 La:1	1170	121	760	1600
224	42.0	6.0	48.0	46.0	0.10	0.10	0.10	Ca:1 Sr:1 Ba:1 La:1	1170	128	2810	1640
225	42.0	6.0	48.0	46.0	0.30	0.10	0.10	Ca:1 Sr:1 Ba:1 La:1	1170	131	1120	1410
226*	42.0	6.0	48.0	46.0	0.40	0.10	0.10	Ca:1 Sr:1 Ba:1 La:1	1170	143	650	1330
227*	42.0	6.0	48.0	46.0	0.10	—	—	Ca:3 Sr:1 Ba:1 La:1	1170	80	2590	2650

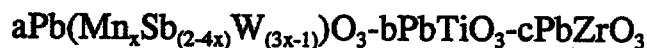
* Examples for comparison according to the prior art

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Date: 14 JUN 1986

What is claimed is :

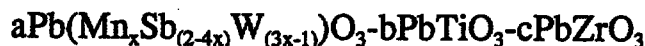
1. A piezoelectric ceramic composition expressed by a general formula :



where a, b, and c represent mol % and are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$, respectively, and $a + b + c = 100$.

2. A piezoelectric ceramic composition according to claim 1, further comprising at least one of magnesium, cobalt, and nickel in a ration of 0.50% or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO , NiO to the piezoelectric ceramic composition.

3. A piezoelectric ceramic composition expressed by a general formula :



where a, b, and c represent mol % and are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$, respectively, and $a + b + c = 100$, wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum.

4. A piezoelectric ceramic composition according to claim 3, wherein up to 5% of lead is replaced by at least one of calcium, strontium, barium, and lanthanum and further comprising at least one of magnesium, cobalt, and nickel in a ration of 0.50% or less by weight in terms of $\text{Mg}(\text{OH})_2$, CoO and NiO .

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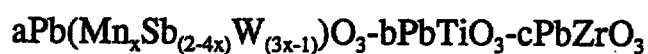
Date: 14 JUN 1996



ABSTRACT OF THE DISCLOSURE

PIEZOELECTRIC CERAMIC COMPOSITIONS

A piezoelectric ceramic composition is expressed by a general formula:



where a, b, and c are in ranges $2 \leq a \leq 10$, $40 \leq b \leq 52$, and $38 \leq c \leq 58$, and $0.35 \leq x \leq 0.48$ respectively (a, b, and c represent mol %, and $a + b + c = 100$). The composition has a large piezoelectric constant and a large mechanical factor of merit, is stable in temperature characteristics, and can be fired at low temperatures.

No figure suggested

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