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(54) PIEZOELECTRIC CERAMIC COMPOSITIONS FOR ACOUSTIC SURFACE WAVE DEVICES

(71) We, MURATA MANUFACTURING CO. LTD., a Corporation of Japan, of No. 16, Kaiden Nishijin-cho, Nagaokakyo-shi, Kyoto-fu, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

This invention relates to piezoelectric materials, in particular piezoelectric ceramics for acoustic surface wave devices such as acoustic surface wave filters, acoustic surface wave delay lines, acoustic surface wave discriminators and the like.

It has been known to use $LiNbO_3$ single crystals, or $LiTaO_3$ single crystals as piezoelectric materials for acoustic surface wave devices. Single crystals of $LiNbO_3$ and $LiTaO_3$ both have the advantage that they have no pores so that it is easy to provide surfaces of single crystal wafers with interdigital electrodes when producing acoustic surface wave filters. Since such single crystals have low permittivity, it is possible to produce acoustic surface wave filters having high impedance, thus making it possible to decrease the matching loss to external electric circuits. Further, such single crystals make it possible to produce acoustic surface wave filters having low propagation loss since their electromechanical coupling factors are relatively high. In addition to the above advantages, the use of single crystal $LiTaO_3$ also makes it possible to produce acoustic surface wave filters having good temperature characteristics since it has a very small temperature coefficient of center frequency of the order of 0 ppm/°C in the temperature range of from – 20°C to + 80°C on the basis of the resonant frequency at a temperature of + 20°C, while single crystal $LiNbO_3$ has a temperature coefficient of the order of – 70 ppm/°C.

Although such single crystals have various advantages as mentioned above, there are serious disadvantages that they are expensive and involve great problems in construction. For example, it is very difficult to cut out single crystal wafers having small values of temperature coefficient of center frequency for acoustic surface wave filters.

Recently, the lead zirconate titanate ceramics have become of major interest as piezoelectric materials for acoustic surface wave devices since such piezoelectric ceramics can be mass produced cheaply by conventional techniques for ceramic manufactures.

Up to now, lead zirconate titanate ceramics have been used as materials for piezoelectric ceramic devices such as ceramic filters, ceramic resonators and ultrasonic wave vibrators. Although the $PbTiO_3$-$PbZrO_3$ solid solutions have two ferroelectric phases, i.e. a ferroelectric tetragonal phase (F_T) and a ferroelectric rhombohedral phase ($F_{R(HT)}$, $F_{R(LT)}$) as shown in Figure 1, the conventionally used $PbTiO_3$-$PbZrO_3$ ceramics are solid solutions of the ferroelectric tetragonal phase for the reason that piezoelectric ceramic devices are generally required to have low temperature dependencies. The use of such a piezoelectric ceramic makes it possible to produce ceramic filters or ceramic resonators having low temperature dependency of center or resonant frequency by the selection of its composition. For example, when a resonator having the radial extensional mode or thickness shear mode is produced by using ceramic of composition $Pb(Ti_{0.55}Zr_{0.45})O_3$, the temperature coefficient of resonant frequency is + 33 ppm/°C or + 21 ppm/°C, respectively, in the temperature range of from - 20°C to + 80°C on the basis of the resonant frequency at + 20°C. On the other hand, the $PbTiO_3$-$PbZrO_3$ solid solutions of the ferroelectric rhombohedral phase have scarcely been used since resonators produced by such ceramics have a large temperature dependency, for example, as can be seen from Figure 2 showing temperature characteristics of resonant frequency for ceramic resonators having the radial extensional mode or thickness

shear mode and consisting of piezoelectric ceramic of composition $Pb(Ti_{0.40}Zr_{0.60})O_3$. In the figure, the temperature characteristic of resonant frequency for the resonator having radial extensional mode is shown by a broken line, and that for a resonator having thickness shear mode is by a dotted line. The change rate of resonant frequency (Δfr) is given by the equation:

$$\Delta fr = \frac{fr - fr20}{fr20}$$

where

fr = Resonant frequency at a temperature in the range of - 20°C to + 80°C
fr 20 = Resonant frequency at 20°C

Accordingly, it will be understood that for the production of acoustic surface wave filters having good temperature characteristics, the use of solid solutions of the ferroelectric tetragonal phase may be preferred. In fact, acoustic surface wave filters of the piezoelectric ceramic of $Pb(Ti_{0.55}Zr_{0.45})O_3$ possess a temperature coefficient of center frequency of the order of + 29 ppm/°C.

However, the ceramics of the solid solution of ferroelectric tetragonal phase have the serious disadvantage that their permittivity is high. In cases where inter-digital electrodes are provided on the surface of ceramic wafers, there exists a relation between the permittivity and impedance which is given by the equation: $|Z| \propto 1/(\epsilon_{33}\epsilon_{11})^{1/2}$. Thus, the greater the permittivity, the smaller the impedance, resulting in increase of matching loss when the acoustic surface wave filter is connected to the external circuit. In order to lessen the matching loss, it is very important to use an acoustic surface wave filter having an impedance nearly equal to the impedance of the external circuit which has generally an impedance of the order of 100 to 1000 ohms. In order to overcome such disadvantages, it has been proposed to reduce the electrostatic capacity between electrodes by dividing the interdigital electrodes perpendicularly to the intersected direction thereof and connecting them in series. However, this necessarily causes an increase in size and cost of the device, which is especially undesirable since the current trend is towards miniaturization and integration of electric circuits.

It is therefore a general object of the present invention to provide new and improved piezoelectric ceramics which make it possible to produce acoustic surface wave devices having a good temperature characteristic, high impedance and a large acoustic surface wave electromechanical coupling factor.

According to the present invention, there are provided piezoelectric ceramics for acoustic surface wave devices, which consist essentially of a solid solution of a lead-titanate-zirconate system, said solid solution being ferroelectric rhombohedral and having a starting point of the phase transition from the stable, low temperature phase to the stable, high temperature phase in the ferroelectric rhombohedral phase at a temperature within the range of from – 20°C + 80°C.

The expression "a solid solution of a lead titanate zirconate system" as used herein includes in particular a lead-titanate-zirconate containing solid solution having a composition represented by the general formula:

$$\sum_{n=1}^{n} a_{n-1}\,(Pb_{1-\alpha_{n-1}}L\alpha_{n-1})\,(M_{n-1}N_{n-1})\,O_3 - yPbTiO_3 - zPbZrO_3$$

wherein a_{n-1}, y and z are the respective mol fractions of the components; the component $(Pb_{1-\alpha_{n-1}}L\alpha_{n-1})(M_{n-1}N_{n-1})O_3$ is a complex oxide having a crystal structure selected from structures of perovskite, complex perovskite compound type pyrochlore, bismuth layer type and tungsten bronze type; L is a metal selected from Ca, Sr, Ba, Li, Na, K, Ag, La, Bi, Cd and Nd; each of M_{n-1} and N_{n-1} is one selected from $Mn_{1/3}$, $Mn_{1/2}$, $Zn_{1/3}$, $Co_{1/3}$, $Ni_{1/3}$, $Ni_{1/2}$, $Fe_{1/3}$, $Fe_{1/2}$, $Sc_{1/2}$, $In_{1/2}$, $Cd_{1/2}$, $Mg_{1/3}$, $Mg_{1/2}$, $Sn_{1/3}$, $Sn_{1/2}$, $Ta_{1/2}$, $Nb_{1/2}$, $Nb_{2/3}$, $Sb_{1/2}$, $Sb_{2/3}$, $W_{1/3}$, $W_{1/2}$, $Cr_{1/2}$, $Sn_{1-\beta}$, $Hf_{1-\beta}$, $Nb_{1-\beta}$, and $Ta_{1-\beta}$ in which $0.00 \leqq \beta < 1.00$; n is an integer from 1 to 4, preferably from 1 to 3; if the sum total $\sum_{n=1}^{n} a_{n-1}$ is represented by x, $x + y + z = 1.00$;

$0.00 \leqq x \leqq 0.40$; $0.05 \leqq y < 0.45$; $0.40 \leqq z \leqq 0.95$; and $0.00 \leqq \alpha_{n-1} \leqq 1.00$.

When n = 1, the lead titanate zirconate containing solid solution is a binary system solid solution having the composition represented by the general formula:

$$yPbTiO_3 - zPbZrO_3$$

wherein $y + z = 1.00$, $0.05 \leqq y \leqq 0.45$, and $0.55 \leqq z \leqq 0.95$.

When n = 2, the lead titanate zirconate containing solid solution is a ternary system solid solution having the composition represented by the general formula:

$$a_1(Pb_{1-\alpha_1}L_{\alpha_1})(M_1N_1)O_3 - yPbTiO_3 - zPbZrO_3$$

wherein $a_1 + y + z = 1.00$, $0.00 < a_1 \leqq 0.40$, $0.05 \leqq y \leqq 0.45$, $0.40 \leqq z \leqq 0.95$, and $0.00 \leqq \alpha_1 \leqq 1.00$. This includes the following compositions where $\alpha_1 = 0$, viz

$a_1\ Pb(Mn\frac{1}{3}\ Nb\frac{2}{3})\ O_3 - y\ PbTiO_3 - z\ PbZrO_3$
$a_1\ Pb(Sn\frac{1}{2}\ Sb\frac{1}{2})\ O_3 - y\ PbTiO_3 - z\ PbZrO_3$
$a_1\ Pb(Sb\frac{1}{2}\ Nb\frac{1}{2})\ O_3 - y\ PbTiO_3 - z\ PbZrO_3$

When n = 3, the lead titanate zirconate containing solid solution is a quaternary system solid solution having the composition represented by the general formula:

$$a_1(Pb_{1-\alpha_1}L_{\alpha_1})O_3 - a_2\ (Pb_{1-\alpha_2})(M_2N_2)O_3 - yPbTiO_3 - zPbZrO_3$$

wherein $x\ (= a_1 + a_2) + y + z = 1.00$, $0.00 < x \leqq 0.40$, $0.05 \leqq y \leqq 0.45$, $0.40 \leqq z \leqq 0.95$, $0.00 \leqq \alpha_1 \leqq 1.00$, and $0.00 \leqq \alpha_2 \leqq 1.00$. An example of such a composition, where α_1 and α_2 are both zero, is given by the general formula $a_1\ Pb\ (Mg\frac{1}{3}\ Nb\ \frac{2}{3})\ O_3 - a_2\ Pb(Sb\frac{1}{2}\ Nb\frac{1}{2})\ O_3 - y\ PbTiO_3 - z\ PbZrO_3$

The or any component $(Pb_{1-\alpha_{n-1}})(M_{n-1}N_{n-1})O_3$ may be one of those listed in Table 1 in which $(Pb_{1-\alpha_{n-1}}L_{\alpha_{n-1}})$ is represented by the symbol A and $(M_{n-1}N_{n-1})$ by the symbol B.

Table 1

Complex oxide Crystal Structure	General Formula	Metal or Compound
Perovskite	$A^{2+}B^{4+}O_3$	A: Pb, Ba, Ca, Sr B: Sn, Hf
	$A^{1+}B^{5+}O_3$	A: Li, Na, K, Ag B: Nb, Ta
Complex Perovskite compound type	$A^{2+}(B_{\frac{1}{3}}^{2+}B_{\frac{2}{3}}^{5+})O_3$	$Pb(Zn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$, $Pb(CO_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$, $Pb(Ni_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$, etc.
	$A^{2+}(B_{\frac{1}{2}}^{3+}B_{\frac{1}{2}}^{5+})O_3$	$Pb(Fe_{\frac{1}{2}}Nb_{\frac{1}{2}})O_3$, $Pb(Sc_{\frac{1}{2}}Ta_{\frac{1}{2}})O_3$, $Pb(In_{\frac{1}{2}}Nb_{\frac{1}{2}})O_3$, etc.
	$A^{2+}(B_{\frac{1}{2}}^{2+}B_{\frac{1}{2}}^{6+})O_3$	$Pb(Cd_{\frac{1}{2}}W_{\frac{1}{2}})O_3$, $Pb(Mg_{\frac{1}{2}}W_{\frac{1}{2}})O_3$, $Pb(Ni_{\frac{1}{2}}W_{\frac{1}{2}})O_3$, etc.
	$A^{2+}(B_{\frac{2}{3}}^{3+}B_{\frac{1}{3}}^{6+})O_3$	$Pb(Fe_{\frac{2}{3}}W_{\frac{1}{3}})O_3$, etc.
	$A^{3+}(B_{\frac{1}{2}}^{2+}B_{\frac{1}{2}}^{4+})O_3$	$La(Mg_{\frac{1}{2}}Ti_{\frac{1}{2}})O_3$, $Nd(Mg_{\frac{1}{2}}Ti_{\frac{1}{2}})O_3$, etc.
	$(A_{\frac{1}{2}}^{1+}A_{\frac{1}{2}}^{3+})BO_3$	$(K_{\frac{1}{2}}La_{\frac{1}{2}})TiO_3$, $(Na_{\frac{1}{2}}Bi_{\frac{1}{2}})TiO_3$, etc.
Pyrochlore	$A_2B_2O_7$	A: Ba, Ca, Sr, Cd, La, Nd B: Ta, Nb, Ti
Bismuth layer type	$Bi_2A_{x-1}B_xO_{3x+3}$	A: Ba, Ca, Sr, Pb B: Ta, Nb, Ti
Tungsten bronze type	$A_xB_2O_6$	A: Pb, Ba, Sr B: Nb, Ta

To the lead titanate zirconate containing solid solution may be added one or more additives selected from MnO_2, NiO, Cr_2O_3, Co_2O_3, SiO_2, Li_2O, Fe_2O_3, WO_3, In_2O_3, MgO, Al_2O_3, V_2O_5, Nb_2O_5, Sb_2O_3, Bi_2O_3, CuO and Ag_2O in an amount not more than 10 wt % with respect to the solid solution to form modified ceramics.

The piezoelectric ceramics of the present invention may be produced by the conventional techniques for ceramic manufactures. If hot pressing is employed, fine piezoelectric ceramics may be obtained.

As mentioned above, the piezoelectric ceramics of the present invention must have the starting point of the phase transition from the stable, low temperature phase ($F_{R(LT)}$) to the stable, high temperature phase ($F_{R(HT)}$) in the ferroelectric rhombohedral phase at a temperature within the range of from – 20°C to + 80°C. Because, if the starting point of the phase transition is present at a temperature outside of the said range, the temperature coefficient of center frequency, for example, of the acoustic surface wave filter, exceeds the permitted value of ± 70 ppm/°C. Thus, it is impossible to produce acoustic surface wave devices having good temperature characteristics..

The phase transition in the ferroelectric rhombohedral phase occurs at the phase boundary between the low temperature phase ($F_{R(LT)}$) and the high temperature phase ($F_{R(HT)}$), and the starting point of phase transition may be observed by X-ray diffraction, or neutron diffraction studies. The starting point of phase transition may also be observed by the measurement of the temperature characteristic of resonant frequency for a resonator having the radial extensional mode since the temperature coefficient of resonant frequency varies abruptly at a temperature where the phase transition occurs. For example, it may be observed from the broken line in Figure 2 showing the temperature characteristic of resonant frequency for the resonator having the radial extensional mode that the solid solution of $Pb(Ti_{0.40}Zr_{0.60})O_3$ has a starting point of phase transition (T_{PT}) at a temperature of – 20°C since the temperature characteristic of resonant frequency varies abruptly at – 20°C.

The invention will be further apparent from the following description with reference to examples and the accompanying drawings, in which;

Figure 1 is a phase diagram for the system $PbTiO_3$-$PbZrO_3$;

Figure 2 is a graph showing the temperature characteristics of resonators having the radial extensional mode or thickness shear mode and consisting of $Pb(Ti_{0.40}Zr_{0.60})O_3$ ceramic;

Figure 3 is a schematic plan view of an acoustic surface wave filter;

Figures 4 and 5 are graphs showing temperature characteristics of center or resonant frequency;

Figure 6 is a graph showing the temperature characteristic of resonant frequency for a resonator having the radial extensional mode; and

Figure 7 is a graph showing the relation between the acoustic surface wave electromechanical coupling factor and the composition of the ceramics.

The compositions and properties of some specific examples of piezoelectric ceramics according to the present invention are shown in the following Table 2 in which asterisks (*) indicate piezoelectric ceramics having compositions outside of the compositional area of the piezoelectric ceramics according to the present invention, either because the solid solution is not piezoelectric rhombohedral or because the starting point of the phase transition from the stable low temperature phase to the stable high temperature phase in the piezoelectric rhombohedral phase does not lie at a temperature within the range of from – 20°C to + 80°C. The symbols T, R, O in the column of crystal phase means a ferroelectric tetragonal phase, a ferroelectric rhombohedral phase and an antiferroelectric orthorhombic phase, respectively.

The raw materials employed for the preparation of the piezoelectric ceramics of the examples were PbO (or Pb_3O_4), TiO_2, ZrO_2, MnO_2 (or $MnCO_3$), Nb_2O_5, SnO_2 and Sb_2O_3, together with the appropriate modifying metal oxides in some cases. In each example, the mixture of powdered raw materials was milled by the wet process for about 10 hours, then the milled mixture was dried and presintered at a temperature of about 700°C to 900°C for 2 hours. The presintered body was crushed, milled by the wet process with an appropriate amount of an organic binder for about 10 hours, dried and passed through a sieve. The resultant powder was shaped into a square wafer having a length of 50 mm and a thickness of 1.2 mm at a pressure of 750 to 1000 kg/cm^2 and then sintered at a temperature of 1150°C to 1300°C for 2 hours in order to obtain a piezoelectric ceramic wafer suitable for elastic surface wave filters.

For better understanding of the present invention, piezoelectric ceramic disks having a diameter of 22 mm and a thickness of 1.2 mm were prepared in the same manner as mentioned above, and used for the preparation of resonators having the radial extensional mode or thickness shear mode.

Table 2

Specimen No.	Basic component (mol ratio)				Additive (%)	crystal phase
	$PbTiO_3$	$PbZrO_3$	ABO_3	ABO_3		
1 ※	0.55	0.45	–	–	–	T
2 ※	0.55	0.45	–	–	MnO_2:0.4	T
3	0.40	0.60	–	–	–	R
4	0.40	0.60	–	–	NiO:0.5	R
5 ※	0.20	0.80	–	–	–	R
6 ※	0.02	0.98	–	–	–	O
7 ※	0.02	0.98	–	–	Cr_2O_3:1.0	O
8 ※	0.50	0.40	$0.10Pb(Mn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$	–	–	T
9 ※	0.50	0.40	$0.10Pb(Mn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$	–	Co_2O_3:0.5	T
10 ※	0.30	0.60	$0.10Pb(Mn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$	–	–	R
11	0.20	0.70	$0.10Pb(Mn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$	–	–	R
12	0.20	0.70	$0.10Pb(Mn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$	–	SiO_2:0.5	R
13	0.20	0.70	$0.10Pb(Mn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$	–	Li_2O:0.5	R
14 ※	0.02	0.88	$0.10Pb(Mn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$	–	Fe_2O_3:0.5	O
15 ※	0.55	0.40	$0.05Pb(Sn_{\frac{1}{2}}Sb_{\frac{1}{2}})O_3$	–	MnO_2:0.4	T
16 ※	0.55	0.40	$0.05Pb(Sn_{\frac{1}{2}}Sb_{\frac{1}{2}})O_3$	–	MnO_2:0.4 WO_3:0.6	T
17	0.35	0.60	$0.05Pb(Sn_{\frac{1}{2}}Sb_{\frac{1}{2}})O_3$	–	MnO_2:0.4	R
18	0.30	0.65	$0.05Pb(Sn_{\frac{1}{2}}Sb_{\frac{1}{2}})O_3$	–	MnO_2:0.4	R
19	0.30	0.65	$0.05Pb(Sn_{\frac{1}{2}}Sb_{\frac{1}{2}})O_3$	–	MnO_2:0.4 Cr_2O_3:1.0	R
20 ※	0.10	0.85	$0.05Pb(Sn_{\frac{1}{2}}Sb_{\frac{1}{2}})O_3$	–	MnO_2:0.4	R
21 ※	0.02	0.93	$0.05Pb(Sn_{\frac{1}{2}}Sb_{\frac{1}{2}})O_3$	–	MnO_2:0.4	O
22 ※	0.02	0.93	$0.05Pb(Sn_{\frac{1}{2}}Sb_{\frac{1}{2}})O_3$	–	MnO_2:0.4 In_2O_3:0.5	O
23	0.20	0.72	$0.04Pb(Mg_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$	$0.04Pb(Sb_{\frac{1}{2}}Nb_{\frac{1}{2}})O_3$	MnO_2:0.4	R

Using the piezoelectric ceramic wafers, there were prepared acoustic surface wave filters in the following manner.

Each piezoelectric ceramic wafer was smoothed on one surface to an extent that the roughness of the surface was not more than 1 μ. Both surfaces of the wafer were provided with electrodes by evaporating gold. The wafer was polarized in an insulating oil maintained at a temperature of 20°C to 200°C, by applying a DC electric field of 3.0 to 4.0 kv/mm. After the polarizing treatment, the wafer was etched to form interdigital electrodes shown in Figure 3 on the smoothed surface. In Figure 3, the dimensions of the electrodes are as follows:

$w = 1.5$ mm, $a = 53\ \mu m$

$d/2 = \lambda/2 = 106\ \mu m$, $\ell = 10$ mm

N (number of pairs of electrodes) = 20

The thus prepared acoustic surface wave filter was subjected to measurement of the acoustic surface wave electromechanical coupling factor (K_{SAW}), the temperature coefficient of center frequency ($C_{fo.SAW}$), the value of $(\varepsilon_{33}\varepsilon_{11})^{1/2}$, and the starting point (or temperature) of the phase transition. The impedance $|Z|$ of the acoustic surface wave filter was calculated from its capacitance.

Using the piezoelectric ceramic disks, there were prepared resonators having the radial extensional mode or thickness shear mode in the following manner.

1. Preparation of resonators having radial extensional mode:

The piezoelectric ceramic disk was provided with a silver electrode on each surface thereof by firing and then polarized in an insulating oil maintained at a temperature of 20°C to 200°C, by applying a DC electric field of 3.0 – 4.0 kv/mm between the electrodes.

The thus prepared resonator was subjected to measurement of permittivity (ϵ_{33}), electromechanical coupling factor (Kp), mechanical quality factor (Qmp) and temperature coefficient of resonant frequency ($C_{fr.p}$).

2. Preparation of resonators having thickness shear mode:

The piezoelectric ceramic disk was ground to a thickness of 200 to 300 μ, provided with a silver electrode on each end thereof of firing, and polarized in an insulating oil maintained at a temperature of 20°C to 200°C, by applying a DC electric field of 3.0 – 4.0 kv/mm between the electrodes. After removal of the silver electrodes, the disk was provided with electrodes on both surfaces thereof by evaporating silver and then etched to form opposed circular electrodes having a diameter of 1 – 2 mm.

The thus prepared thickness shear mode resonator was also subjected to measurement of piezoelectric properties such as the permittivity (ϵ_{11}), electromechanical coupling factor (K_{15}), mechanical quality factor (Qm_{15}), and temperature coefficient of resonant frequency ($C_{fr.15}$).

The results are shown in Table 3.

The acoustic surface wave electromechanical coupling factor (K_{saw}) is given by the following equation:

$$(V_2-V_1)/V_1 = 1 - \sqrt{1 + (K_{SAW})^2} \cong -\tfrac{1}{2}(K_{SAW})^2$$

where

V_1 = acoustic surface wave velocity in the case that no gold layer is provided on the propagation path.

V_2 = acoustic surface wave velocity in the case that a conductive gold layer is provided on the propagation path.

The measurements of permittivity (ϵ_{33}), (ϵ_{11})

Table 3

Specimen No.		Resonator with radial extensional mode				Resonator with thickness shear mode			Acoustic surface wave filter				
		ϵ_{33} (at 1 KHz)	Kp	Qmp	Cfr.p	ϵ_{11} (at 1 KHz)	K_{15}	Qm_{15}	$Crf._{15}$	K_{SAW}	$Cfo._{SAW}$	½ ($\epsilon_{33}\epsilon_{11}$)	Z (Ω)	Starting point
1	※	583	30	452	+33	768	34	182	+21	12.3	+29	669	86	—
2	※	574	32	1215	+28	784	35	413	+18	11.5	+30	671	85	—
3		403	35	474	+182	544	58	195	−150	17.0	+25	468	141	−20°C
4		374	33	939	+177	471	55	310	−148	16.8	−26	419	172	−20°C
5	※	349	17	689	−158	476	34	233	−83	16.0	−83	408	184	120°C
6	※	182	0	0	—	—	—	—	—	—	—	—	—	—
7	※	170	0	0	—	—	—	—	—	—	—	—	—	—
8	※	739	46	2161	+20	973	60	750	+25	17.0	+27	848	69	—
9	※	714	45	2533	+18	988	61	888	+19	17.2	+15	840	72	—
10	※	323	28	6552	−79	586	45	1205	−154	17.0	−85	435	157	−100°C
11		267	18	5418	+208	459	38	915	−77	16.8	+28	350	201	20°C

Table 3 – continued

Specimen No.		Resonator with radial extensional mode				Resonator with thickness shear mode				Acoustic surface wave filter				
		ϵ_{33} (at 1 KHz)	Kp	Qmp	Cfr.p	ϵ_{11} (at 1 KHz)	K_{15}	Qm_{15}	$Crf._{15}$	K_{SAW}	$Cfo._{SAW}$	½ ($\epsilon_{33}\epsilon_{11}$)	Z (Ω)	Starting point
12		254	19	4335	+215	473	39	871	–73	14.7	+33	347	206	20°C
13		268	20	5634	+187	486	40	1105	–71	15.2	+21	360	193	20°C
14	※	219	0	0	–	–	–	–	–	–	–	–	–	–
15	※	677	30	1956	–29	892	36	644	–37	13.6	–27	777	80	–
16	※	703	33	1721	–25	875	38	550	–33	14.0	–25	784	78	–
17		363	30	2625	+160	670	51	514	–138	16.2	+38	493	130	–20°C
18		329	22	3249	+161	584	46	747	–59	16.0	+25	438	153	40°C
19		311	24	2890	+186	597	47	703	–66	16.1	–30	431	155	40°C
20	※	246	13	4797	–245	373	38	1157	–81	15.3	–93	302	220	90°C
21	※	193	0	0	–	–	–	–	–	–	–	–	–	–
22	※	218	0	0	–	–	–	–	–	–	–	–	–	–
23		325	19	4837	+223	606	42	877	–100	15.0	+13	444	150	60°C

were made with a capacitance bridge, and the electromechanical coupling factors (Kp), (K_{15}) and mechanical quality factors (Qmp), (Q_{m15}) were measured with IRE standard circuits.

The temperature coefficient of center frequency or resonant frequency is given by the following equation:

Temperature coefficient ($C_{fo.SAW}$, $C_{fr.p}$, $C_{fr.15}$)

$$\text{where} = \frac{f_{max} - f_{min}}{f_{20}} \times \frac{1}{100}$$

f_{20} = center (or resonant) frequency at 20°C

f_{max} = maximum value of center (or resonant) frequency at a temperature within the range of – 20°C to + 80°C.

f_{min} = minimum value of center (or resonant) frequency at a temperature within the range of – 20°X to + 80°C.

As can be seen from the results shown in Table 3, the resonators having the radial extensional mode or thickness shear mode and consisting of plain or modified ceramics of the ferroelectric rhombohedral solid solutions are inferior to the resonators consisting of ceramics of the ferroelectric tetragonal solid solutions in the temperature coefficient of resonant frequency. However, when ceramics of ferroelectric rhombohedral solid solution are adapted as acoustic surface wave filters, it is possible to produce acoustic surface wave filters having good temperature characteristics since the temperature coefficients of resonant frequency for radial extensional mode and thickness shear mode combine so as to compensate for each other. This is supported by the experimental data for the acoustic surface wave filters in Table 3. For example, specimens Nos. 17 and 18 have good temperature characteristics as shown in Figures 4 and 5, respectively, in which solid lines show temperature characteristics of center frequency for acoustic surfaces wave filters, broken lines show the temperature characteristics of resonant frequency for resonators having radial extensional mode vibration, and dotted lines show the temperature characteristics of resonant frequency for resonators having thickness shear mode.

However, it has been found that not all the piezoelectric ceramics having compositions of the ferroelectric rhombohedral phase necessarily possess good temperature characteristics of center frequency. It has also been found that, in order to produce acoustic surface wave filters having good temperature characteristics, the ceramics are required to have a starting point of the phase transition from the stable low temperature phase ($F_{R(LT)}$) to the stable high temperature phase ($F_{R(HT)}$) in the ferroelectric rhombohedral phase within the temperature range of -20°C to + 80°C. If the starting point of the phase transition is present outside the above temperature range it is difficult to produce acoustic surface wave filters having good temperature coefficient of center frequency. Figure 6 shows the temperature characteristics of resonant frequency for resonators each having the radial extensional mode and consisting of the ceramics of specimens Nos. 5 and 10. In the figure, the solid line shows the temperature characteristic of resonant frequency for the resonator of ceramics of the specimen No. 5, and the broken line shows the temperature characteristic of resonant frequency for the resonator of the ceramics of the specimen No. 10. As can be seen from Table 3, when ceramics of the specimens Nos. 5 and 10 are adapted as acoustic surface wave filters, the temperature coefficients of center frequency thereof are - 83 ppm/°C and - 85 ppm/°C, respectively, which are greater than the permitted value of ± 70 ppm/°C.

As mentioned above, acoustic surface wave filters are required to have high impedance to minimise the matching loss to the external circuit. This requirement is fully met by the use of the piezoelectric ceramics of the present invention since the acoustic surface wave filters comprising the piezoelectric ceramics of the present invention have high impedance greater by 150 to 300 % than those comprising piezoelectric ceramics having the compositions of the ferroelectric tetragonal phase.

The piezoelectric ceramics according to the present invention have further advantage that they make it possible to produce acoustic surface wave filters having large acoustic surface wave electromechanical coupling factors. Figure 7 shows the relation between the acoustic surface wave electromechanical coupling factor and the composition of the ceramics used. As can be seen from the figure, the ceramics having compositions of the ferroelectric rhombohedral phase possess large acoustic surface wave electromechanical coupling factors over a wider range of composition, compared with the ceramics having the compositions of the ferroelectric tetragonal phase, and the change rate of the acoustic surface wave electromechanical coupling coefficient with variation of composition is very small.

It has been observed that the piezoelectric ceramics of the present invention having the composition of the ferroelectric rhombohedral phase at room temperature have a smaller change rate of acoustic surface wave velocity with variation of the composition than to

piezoelectric ceramics having the composition of the ferroelectric tetragonal phase at room temperature.

Although the invention has been described with respect to acoustic surface wave filters, the piezoelectric ceramics of the present invention may be used as materials for other acoustic surface wave devices such as acoustic surface wave delay lines and acoustic surface wave discriminators.

WHAT WE CLAIM IS:–

1. Piezoelectric ceramics for acoustic surface wave devices, which consist essentially of a solid solution of a lead-titanate zirconate system, said solid solution being ferroelectric rhombohedral and having a starting point of the phase transition from the stable low temperature phase to the stable high temperature phase in the ferroelectric rhombohedral phase at a temperature within the range of from – 20°C to + 80°C.

2. The piezoelectric ceramics according to claim 1 wherein said solid solution of a lead titanate zirconate system is a lead titanate zirconate containing solid solution having a composition represented by the general formula:

$$\sum_{n=1}^{n} a_{n-1}(Pb_{1-\alpha_{n-1}}L_{\alpha_{n-1}})(M_{n-1}N_{n-1})O_3 - yPbTiO_3 - zPbZrO_3$$

wherein a_{n-1}, y and z are the respective mol fractions of the components, the component $(Pb_{1-\alpha_{n-1}}L_{\alpha_{n-1}})(M_{n-1}N_{n-1})O_3$ is a complex oxide having the crystal structure selected from structures of perovskite, complex perovskite compound type pyrochlore, bismuth layer type and tungsten bronze type; L is one metal selected from Ca, Sr, Ba, Li, Na, K, Ag, La, Bi, Cd and Nd; each of M_{n-1} and N_{n-1} is one selected from $Mn_{1/3}$, $Mn_{1/2}$, $Zn_{1/3}$, $Co_{1/3}$, $Ni_{1/3}$, $Ni_{1/2}$, $Fe_{1/3}$, $Fe_{1/2}$, $Sc_{1/2}$, $In_{1/2}$, $Cd_{1/2}$, $Mg_{1/3}$, $Mg_{1/2}$, $Sn_{1/3}$, $Sn_{1/2}$, $Ta_{1/2}$, $Nb_{1/2}$, $Nb_{2/3}$, $Sb_{1/2}$, $Sb_{2/3}$, $W_{1/3}$, $W_{1/2}$, $Cr_{1/2}$, $Sn_{1-\beta}$, $Hf_{1-\beta}$, $Nb_{1-\beta}$ and $Ta_{1-\beta}$ in which $0.00 < \beta < 1.00$; n is an integer from 1 to 4, if the sum total

$\sum_{n=1}^{n} a_{n-1}$ is represented by x, $x + y + y\,z = 1.00$; $0.00 < x < 0.40$;

$0.05 \leqq y \leqq 0.45$; $0.40 \leqq z \leqq 0.95$; and $0.00 \leqq \alpha_{n-1} \leqq 1.00$.

3. The piezoelectric ceramics according to claim 2, wherein n is an integer from 1 to 3.

4. The piezoelectric ceramics according to claim 1 wherein n = 1 and said lead titanate zirconate containing solid solution is a binary system solid solution having the composition represented by the general formula:

$$yPbTiO_3 - zPbZrO_3$$

wherein $y + z = 1.00$, $0.05 \leqq y \leqq 0.45$, and $0.55 \leqq z \leqq 0.95$

5. The piezoelectric ceramics according to claim 2 wherein n = 2 and said lead titanate zirconate containing solid solution is a ternary system solid solution having the composition represented by the general formula:

$$a_1(Pb_{1-\alpha_1}L_{\alpha_1})(M_1N_1)O_3 - yPbTiO_3 - zPbZrO_3$$

wherein $a_1 + y + z = 1.00$, $0.00 \leqq a_1 \leqq 0.40$, $0.05 \leqq y \leqq 0.45$, $0.40 \leqq z \leqq 0.95$, and $0.00 \leqq \alpha_1 \leqq 1.00$.

6. The piezoelectric ceramics according to claim 5 wherein said lead titanate zirconate containing solid solution is a ternary system solid solution having the composition represented by the general formula:

$$a_1Pb(Mn_{1/3}Nb_{2/3})O_3 - yPbTiO_3 - zPbZrO_3$$

7. The piezoelectric ceramics according to claim 5 wherein said lead titanate zirconate containing solid solution is a ternary system solid solution having the composition represented by the general formula:

$$a_1Pb(Sn_{1/2}Sb_{1/2})O_3 - yPbTiO_3 - zPbZrO_3$$

8. The piezoelectric ceramics according to claim 5 wherein said lead titanate zirconate containing solid solution is a ternary system solid solution having the composition represented by the general formula:

$$a_1Pb(Sb_{1/2}Nb_{1/2})O_3 - yPbTiO_3 - zPbZrO_3$$

piezoelectric ceramics having the composition of the ferroelectric tetragonal phase at room temperature.

Although the invention has been described with respect to acoustic surface wave filters, the piezoelectric ceramics of the present invention may be used as materials for other acoustic surface wave devices such as acoustic surface wave delay lines and acoustic surface wave discriminators.

WHAT WE CLAIM IS:–

1. Piezoelectric ceramics for acoustic surface wave devices, which consist essentially of a solid solution of a lead-titanate zirconate system, said solid solution being ferroelectric rhombohedral and having a starting point of the phase transition from the stable low temperature phase to the stable high temperature phase in the ferroelectric rhombohedral phase at a temperature within the range of from – 20°C to + 80°C.

2. The piezoelectric ceramics according to claim 1 wherein said solid solution of a lead titanate zirconate system is a lead titanate zirconate containing solid solution having a composition represented by the general formula:

$$\sum_{n=1}^{n} a_{n-1}(Pb_{1-\alpha_{n-1}}L_{\alpha_{n-1}})(M_{n-1}N_{n-1})O_3 - yPbTiO_3 - zPbZrO_3$$

wherein a_{n-1}, y and z are the respective mol fractions of the components, the component $(Pb_{1-\alpha_{n-1}}L_{\alpha_{n-1}})(M_{n-1}N_{n-1})O_3$ is a complex oxide having the crystal structure selected from structures of perovskite, complex perovskite compound type pyrochlore, bismuth layer type and tungsten bronze type; L is one metal selected from Ca, Sr, Ba, Li, Na, K, Ag, La, Bi, Cd and Nd; each of M_{n-1} and N_{n-1} is one selected from $Mn_{1/3}$, $Mn_{1/2}$, $Zn_{1/3}$, $Co_{1/3}$, $Ni_{1/3}$, $Ni_{1/2}$, $Fe_{1/3}$, $Fe_{1/2}$, $Sc_{1/2}$, $In_{1/2}$, $Cd_{1/2}$, $Mg_{1/3}$, $Mg_{1/2}$, $Sn_{1/3}$, $Sn_{1/2}$, $Ta_{1/2}$, $Nb_{1/2}$, $Nb_{2/3}$, $Sb_{1/2}$, $Sb_{2/3}$, $W_{1/3}$, $W_{1/2}$, $Cr_{1/2}$, $Sn_{1-\beta}$, $Hf_{1-\beta}$, $Nb_{1-\beta}$ and $Ta_{1-\beta}$ in which $0.00 < \beta < 1.00$; n is an integer from 1 to 4, if the sum total

$\sum_{n=1}^{n} a_{n-1}$ is represented by x, $x + y + y\,z = 1.00$; $0.00 < x < 0.40$;

$0.05 \leqq y \leqq 0.45$; $0.40 \leqq z \leqq 0.95$; and $0.00 \leqq \alpha_{n-1} \leqq 1.00$.

3. The piezoelectric ceramics according to claim 2, wherein n is an integer from 1 to 3.

4. The piezoelectric ceramics according to claim 1 wherein n = 1 and said lead titanate zirconate containing solid solution is a binary system solid solution having the composition represented by the general formula:

$$yPbTiO_3 - zPbZrO_3$$

wherein $y + z = 1.00$, $0.05 \leqq y \leqq 0.45$, and $0.55 \leqq z \leqq 0.95$

5. The piezoelectric ceramics according to claim 2 wherein n = 2 and said lead titanate zirconate containing solid solution is a ternary system solid solution having the composition represented by the general formula:

$$a_1(Pb_{1-\alpha_1}L_{\alpha_1})(M_1N_1)O_3 - yPbTiO_3 - zPbZrO_3$$

wherein $a_1 + y + z = 1.00$, $0.00 \leqq a_1 \leqq 0.40$, $0.05 \leqq y \leqq 0.45$, $0.40 \leqq z \leqq 0.95$, and $0.00 \leqq \alpha_1 \leqq 1.00$.

6. The piezoelectric ceramics according to claim 5 wherein said lead titanate zirconate containing solid solution is a ternary system solid solution having the composition represented by the general formula:

$$a_1Pb(Mn_{1/3}Nb_{2/3})O_3 - yPbTiO_3 - zPbZrO_3$$

7. The piezoelectric ceramics according to claim 5 wherein said lead titanate zirconate containing solid solution is a ternary system solid solution having the composition represented by the general formula:

$$a_1Pb(Sn_{1/2}Sb_{1/2})O_3 - yPbTiO_3 - zPbZrO_3$$

8. The piezoelectric ceramics according to claim 5 wherein said lead titanate zirconate containing solid solution is a ternary system solid solution having the composition represented by the general formula:

$$a_1Pb(Sb_{1/2}Nb_{1/2})O_3 - yPbTiO_3 - zPbZrO_3$$

9. The piezoelectric ceramics according to claim 2 wherein n = 3 and said lead titanate zirconate containing solid solution is a quaternary system solid solution having the composition represented by the general formula:

$$a_1(Pb_{1-\alpha_1}L_{\alpha_1})(M_1N_1)O_3 - a_2(Pb_{1-\alpha_2}L_{\alpha_2})(M_2N_2)O_3 - yPbTiO_3 - zPbZrO_3$$

wherein $x\ (=a_1+a_2)+a_2) + y + z = 1.00$, $0.00 < x \leqq 0.40$, $0.05 \leqq y \leqq 0.45$, $0.40 \leqq z \leqq 0.95$, $0.00 \leqq \alpha_1 \leqq 1.00$, and $0.00 \leqq \alpha_1 \leqq 1.00$.

10. The piezoelectric ceramics according to claim 9 wherein said lead titanate zirconate containing solid solution is a quaternary system solid solution having the composition represented by the general formula:

$$a_1Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}a_2Pb(Sb_{1/2}Nb_{1/2})O_3\text{-}yPbTiO_3 - zPbZrO_3$$

11. The piezoelectric ceramics according to any one of the preceding claims wherein to said lead titanate zirconate containing solid solution is added one or more additives selected from MnO_2, NiO, Cr_2O_3, Co_2O_3, SiO_2, Li_2O, Fe_2O_3, WO_3, In_2O_3, MgO, Al_2O_3, V_2O_5, Nb_2O_5, Sb_2O_3, Bi_2O_3, Mo_2O_3, CuO and Ag_2O in an amount not more than 10 wt% with respect to the said solid solution.

12. Any one of the piezoelectric ceramics according to claim 1 which are specifically exemplified herein.

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