

FIG. 1

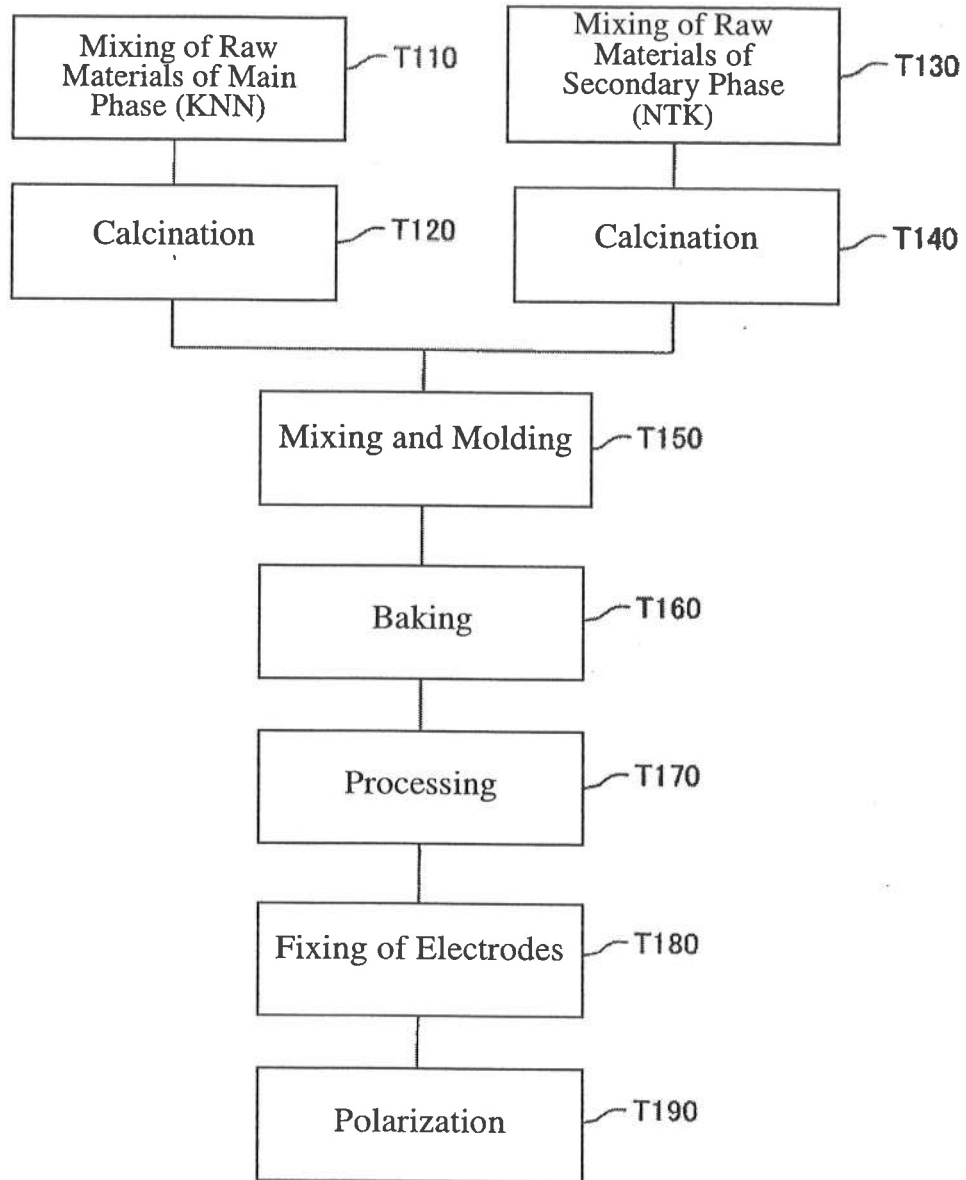


FIG. 2

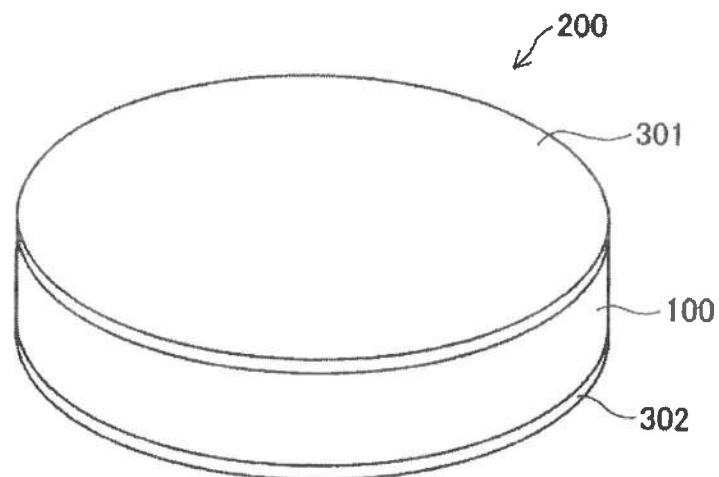


FIG. 3A

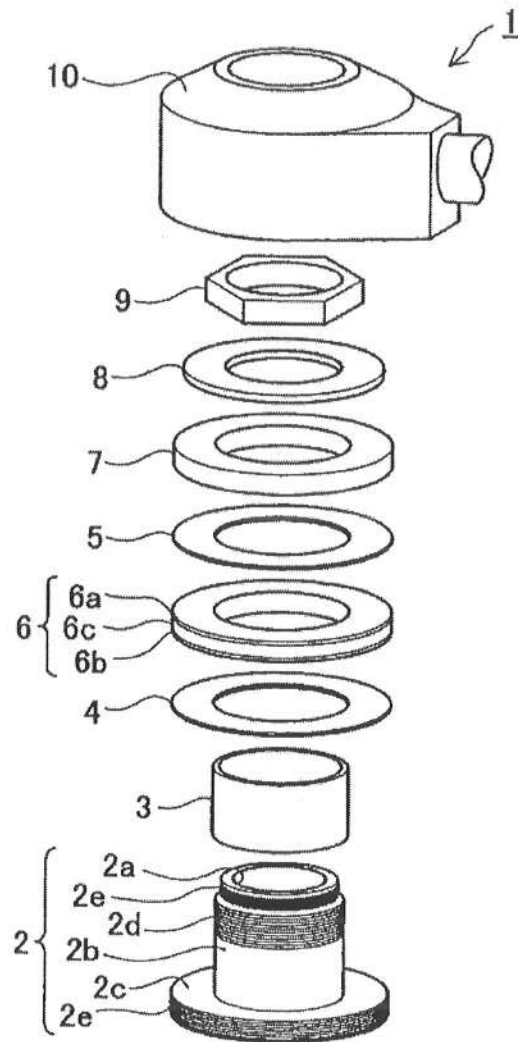


FIG. 3B

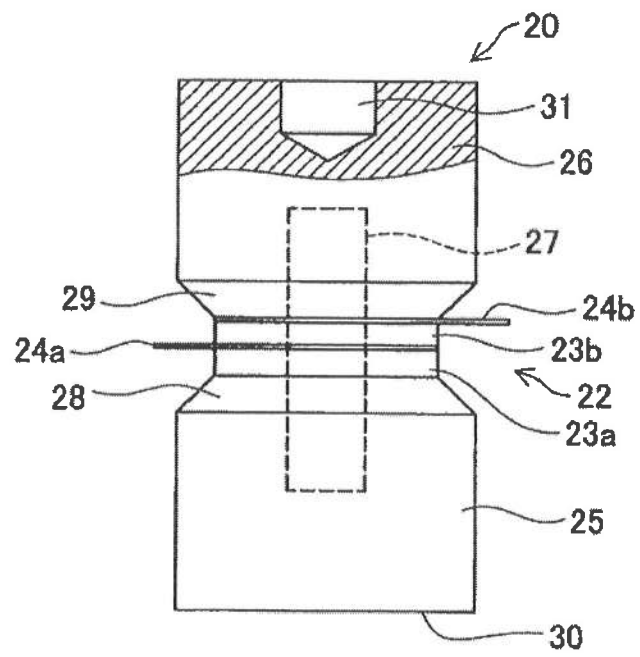


FIG. 3C

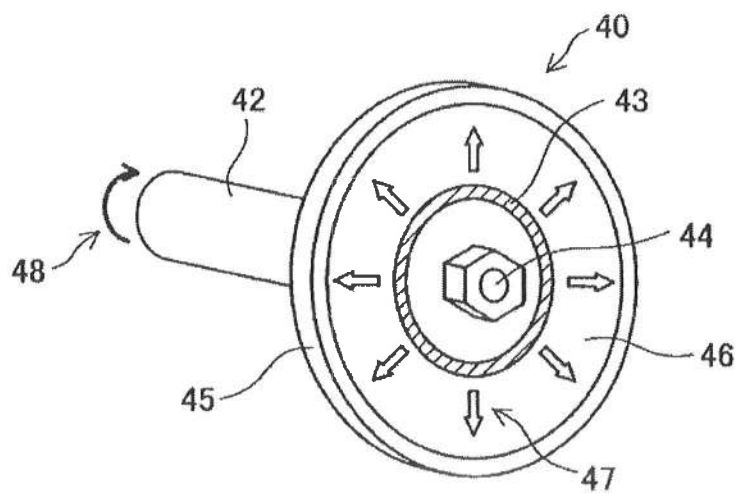


FIG. 4

Sample	First crystal phase (main phase)						Second crystal phase (secondary phase)			Content of secondary phase (mol%)	Relative dielectric constant $\epsilon_{33}^T/\epsilon_0$	Piezoelectric constant d_{33} (pC/N)	Electro- mechanical coupling factor k_r
	Element C	Element B	a	b	c	d	e	f	Element A	Element B	x		
S01	—	—	—	—	—	—	—	—	K	Nb	0	—	—
S02	—	—	—	—	—	—	—	—	K	Nb	0.15	—	—
S03	—	Nb	0.500	0.500	0	0	1.00	3.00	—	—	—	90	0.30
S04	—	Nb	0.490	0.490	0.020	0	1.00	3.00	—	—	—	95	0.31
S05	—	Nb	0.490	0.490	0.020	0	1.00	3.00	K	Nb	0	154	0.36
S06	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	120	0.30
S07	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	164	0.32
S08	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	170	0.43
S09	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	163	0.35
S10	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	120	0.31
S11	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	105	0.30
S12	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	60	0.20
S13	Ca	Nb	0.455	0.474	0.022	0.049	1.07	3.06	K	Ta	0	153	0.35
S14	Ca	Nb	0.455	0.474	0.022	0.049	1.07	3.06	K	Nb	0.15	155	0.38
S15	Ca, Sr	Nb	0.420	0.519	0.022	0.039	1.07	3.06	K	Nb	0	120	0.31

First crystal phase (main phase): $(K_aNa_bLi_cCa_d)_{2f}DO_f$

(C: at least one of Ca, Sr and Ba, D: at least one of Nb and Ta, $a+b+c+d=1$, e: an arbitrary value, f: an arbitrary value that constitutes a perovskite structure)

Second crystal phase (secondary phase): $A_{1-x}Ti_{1-x}B_{1+x}O_5$

(A: at least one kind of alkali metal, B: at least one of Nb and Ta, x: an arbitrary value)

FIG. 5

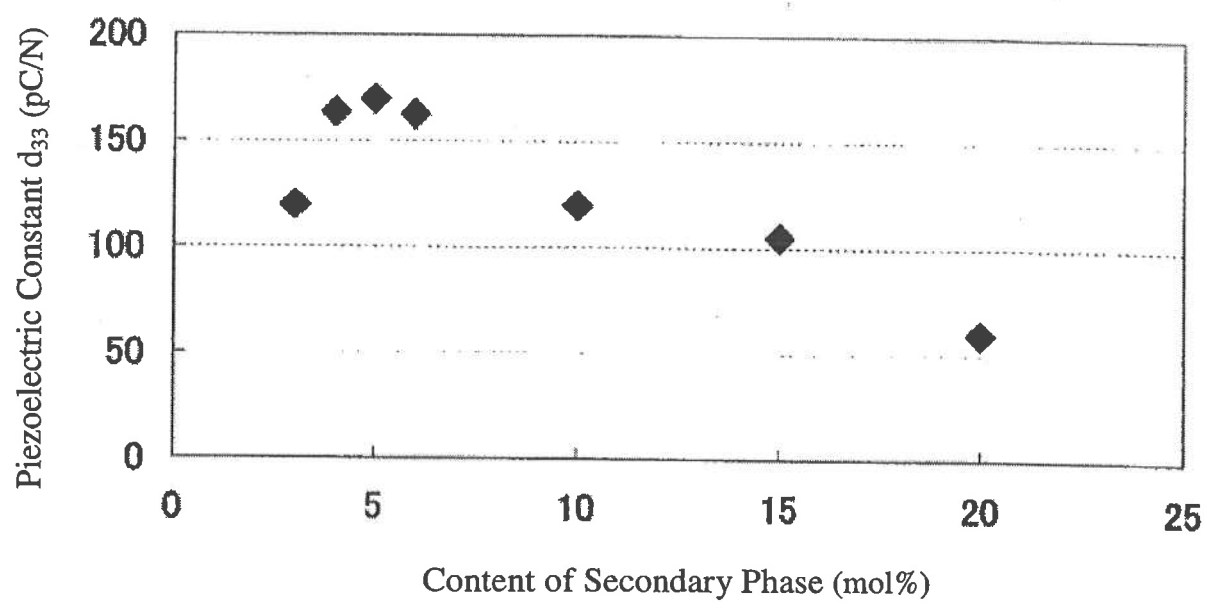


FIG. 6

Sample	First crystal phase (main phase)							Second crystal phase (secondary phase)			Content of secondary phase (mol%)	Curie point T _c (°C)	Room-temperature phase transition
	Element C	Element B	a	b	c	d	e	f	Element A	Element B	x		
S01	—	—	—	—	—	—	—	—	K	Nb	0	—	—
S02	—	—	—	—	—	—	—	—	K	Nb	0.15	—	—
S03	—	Nb	0.500	0.500	0	0	1.00	3.00	—	—	—	400	occurred
S04	—	Nb	0.490	0.490	0.020	0	1.00	3.00	—	—	—	410	occurred
S05	—	Nb	0.490	0.490	0.020	0	1.00	3.00	K	Nb	0	340	not occurred
S06	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	350	not occurred
S07	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	350	not occurred
S08	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	350	not occurred
S09	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	350	not occurred
S10	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	350	not occurred
S11	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	350	not occurred
S12	Ca	Nb	0.421	0.518	0.022	0.039	1.07	3.06	K	Nb	0.15	350	not occurred
S13	Ca	Nb	0.455	0.474	0.022	0.049	1.07	3.06	K	Ta	0	300	not occurred
S14	Ca	Nb	0.455	0.474	0.022	0.049	1.07	3.06	K	Nb	0.15	350	not occurred
S15	Ca, Sr	Nb	0.420	0.519	0.022	0.039	1.07	3.06	K	Nb	0	340	not occurred

First crystal phase (main phase): $(K_eNa_bLi_cC_d)_2DO_f$

(C: at least one of Ca, Sr and Ba, D: at least one of Nb and Ta, $a+b+c+d=1$, e: an arbitrary value, f: an arbitrary value that constitutes a perovskite structure)

Second crystal phase (secondary phase): $A_{1-x}Ti_{1-x}B_{1+x}O_5$

(A: at least one kind of alkali metal, B: at least one of Nb and Ta, x: an arbitrary value)

FIG. 7

Sample	First crystal phase (main phase)					Second crystal phase (secondary phase)			Content of secondary phase (mol%)	Relative dielectric constant $\epsilon_{33}^T/\epsilon_0$	Piezoelectric constant d_{33} (pC/N)	Electro- mechanical coupling factor k_r
	a	b	c	d	e	f	Element A	Element B	x			
S04	0.490	0.490	0.020	0	1.00	3.00	—	—	—	430	95	0.31
S21	0.455	0.474	0.022	0.049	0.970	3.01	K	Nb	0	880	105	0.29
S22	0.455	0.474	0.022	0.049	1.000	3.02	K	Nb	0.15	1040	139	0.36
S23	0.455	0.474	0.022	0.049	1.035	3.04	K	Nb	0.15	1110	157	0.40
S24	0.455	0.474	0.022	0.049	1.049	3.05	K	Nb	0.15	1060	167	0.42
S25 (S14)	0.455	0.474	0.022	0.049	1.070	3.06	K	Nb	0.15	1200	155	0.38
S26	0.455	0.474	0.022	0.049	1.089	3.07	K	Nb	0.15	1100	47	0.12
S27	0.455	0.474	0.022	0.049	1.100	3.08	K	Nb	0.15	1090	45	0.12

First crystal phase (main phase): $(K_eNa_bLi_cCa_d)_eNbO_f$

($a+b+c+d = 1$, e : an arbitrary value, f : an arbitrary value that constitutes a perovskite structure)

Second crystal phase (secondary phase): $A_{1-x}Ti_{1-x}B_{1+x}O_5$

(A: at least one kind of alkali metal, B: at least one of Nb and Ta, x : an arbitrary value)

FIG. 8

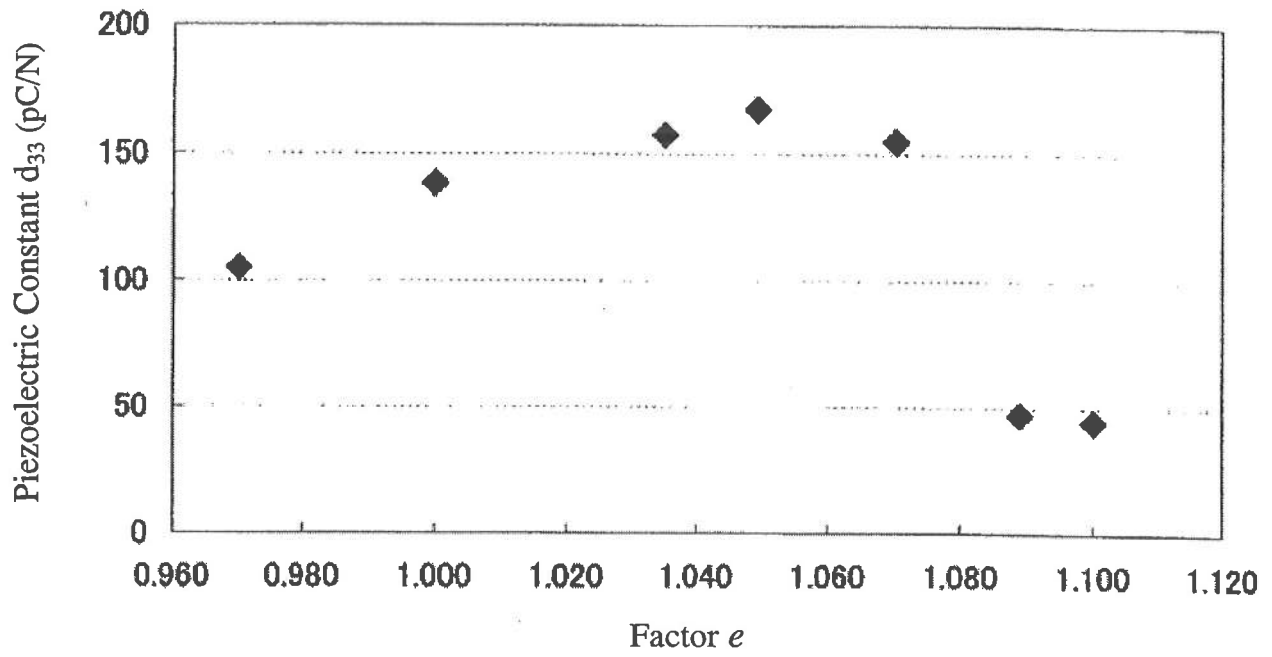


FIG. 9

Sample	First crystal phase (main phase)						Second crystal phase (secondary phase)			Content of secondary phase (mol%)	Additive metal		Relative dielectric constant $\epsilon_{33}^T/\epsilon_0$	Piezoelectric constant d_{33} (pC/N)	Electro- mechanical coupling factor k_r
	a	b	c	d	e	f	Element A	Element B	x		Metal	mol%			
S04	0.490	0.490	0.020	0	1.00	3.00	—	—	—	0	—	0	430	95	0.31
S31	0.500	0.500	0	0	1.000	3.00	—	—	—	0	Cu	1	235	95	0.37
S32 (S08)	0.421	0.518	0.022	0.039	1.070	3.06	K	Nb	0.15	5	—	0	1130	170	0.43
S33	0.455	0.484	0.022	0.039	1.070	3.06	K	Nb	0.15	5	Cu	0.5	1050	186	0.46
S34	0.455	0.484	0.022	0.039	1.070	3.06	K	Nb	0.15	5	Cu	1	985	138	0.38
S35	0.455	0.484	0.022	0.039	1.070	3.06	K	Nb	0.15	5	Cu Fe	0.5 0.5	1042	200	0.48
S36	0.464	0.474	0.022	0.039	1.070	3.06	K	Nb	0.15	5	Fe	0.5	1119	199	0.48
S37	0.464	0.474	0.022	0.039	1.070	3.06	K	Nb	0.15	5	Cu Ni	0.5 0.5	1150	170	0.44
S38	0.464	0.474	0.022	0.039	1.070	3.06	K	Nb	0.15	5	Ag	0.5	1060	171	0.42
S39	0.464	0.474	0.022	0.039	1.070	3.06	K	Nb	0.15	5	Zr	0.5	1121	166	0.42
S40	0.464	0.474	0.022	0.039	1.070	3.06	K	Nb	0.15	5	Zn	0.5	1221	175	0.42
S41	0.464	0.474	0.022	0.039	1.070	3.06	K	Nb	0.15	5	Sc Bi	0.5 0.5	1213	172	0.41
S42	0.464	0.474	0.022	0.039	1.070	3.06	K	Nb	0.15	5	Mn	0.5	976	156	0.42
S43	0.455	0.474	0.022	0.049	1.070	3.06	K	Nb	0.15	5	Co	0.5	1080	180	0.45

First crystal phase (main phase): $(K_aNa_bLi_cCa_d)_eNbO_f$

($a+b+c+d=1$, e : an arbitrary value, f : an arbitrary value that constitutes a perovskite structure)

Second crystal phase (secondary phase): $A_{1-x}Ti_{1-x}B_{1+x}O_5$

(A: at least one kind of alkali metal, B: at least one of Nb and Ta, x : an arbitrary value)

FIG. 10

Sample	First crystal phase (main phase)					Second crystal phase (secondary phase)			Content of secondary phase (mol%)	Additive metal		Applicable voltage ^{cf.)} (kV/mm)
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	Element A	Element B		Metal	mol%	
S03	0.500	0.500	0	0	1.00	3.00	—	—	0	—	0	3
S04	0.490	0.490	0.020	0	1.00	3.00	—	—	0	—	0	3
S08	0.421	0.518	0.022	0.039	1.070	3.06	K	Nb	5	—	0	7
S35	0.455	0.484	0.022	0.039	1.070	3.06	K	Nb	5	Cu, Fe	0.5, 0.5	9

First crystal phase (main phase): $(K_aNa_bLi_cCa_d)_eNbO_f$

($a+b+c+d = 1$, e : an arbitrary value, f : an arbitrary value that constitutes a perovskite structure)

Second crystal phase (secondary phase): $A_{1-x}Ti_{1-x}B_{1+x}O_5$

(A: at least one kind of alkali metal, B: at least one of Nb and Ta, x : an arbitrary value)

cf.) Measurement conditions: 80°C, 30 min.

FIG. 11

The case of mixing KTiNbO_5 phase as second crystal phase

Sample	First crystal phase (main phase)						Content of secondary phase (mol%)	Additive metal		NTK phase (XRD)	NTK phase (TEM-EDS)
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>		Metal	mol%		
S06 (FIG. 4)	0.421	0.518	0.022	0.039	1.070	3.06	3	—	0	—	1115
S08 (FIG. 4)	0.421	0.518	0.022	0.039	1.070	3.06	5	—	0	1115	1115
S10 (FIG. 4)	0.421	0.518	0.022	0.039	1.070	3.06	10	—	0	1115	1115
S12 (FIG. 4)	0.421	0.518	0.022	0.039	1.070	3.06	20	—	0	1115	1115
S33 (FIG. 9)	0.455	0.484	0.022	0.039	1.070	3.06	5	Cu,	0.5	—	1115
S35 (FIG. 9)	0.455	0.484	0.022	0.039	1.070	3.06	5	Cu, Fe	0.5, 0.5	1319	1319
S36 (FIG. 9)	0.464	0.474	0.022	0.039	1.070	3.06	5	Fe	0.5	1319	1319
S40 (FIG. 9)	0.464	0.474	0.022	0.039	1.070	3.06	5	Zn	0.5	1115	1115
S42 (FIG. 9)	0.464	0.474	0.022	0.039	1.070	3.06	5	Mn	0.5	1115, 1319	1115, 1319

First crystal phase (main phase): $(\text{K}_a\text{Na}_b\text{Li}_c\text{Ca}_d)_e\text{NbO}_f$

($a+b+c+d=1$, e : an arbitrary value, f : an arbitrary value that constitutes a perovskite structure)

Second crystal phase (secondary phase):

NTK phase: 1115 KTiNbO_5 phase

NTK phase: 1319 KTi_3NbO_9 phase

FIG. 12

The case of mixing KTi_3NbO_9 phase as second crystal phase

Sample	First crystal phase (main phase)						Content of secondary phase (mol%)	Additive metal		NTK phase (XRD)	NTK phase (TEM-EDS)
	a	b	c	d	e	f		Metal	mol%		
S51	0.421	0.518	0.022	0.039	1.070	3.06	3	—	0	—	1319
S52	0.421	0.518	0.022	0.039	1.070	3.06	5	—	0	1319	1319
S53	0.455	0.484	0.022	0.039	1.070	3.06	5	Cu	0.5	—	1319
S54	0.455	0.484	0.022	0.039	1.070	3.06	5	Cu, Fe	0.5, 0.5	1319	1319
S55	0.421	0.518	0.022	0.039	1.070	3.06	5	Fe	0.5	1319	1319
S56	0.421	0.508	0.022	0.049	1.070	3.07	5	Zn	0.5	1319	1319
S57	0.416	0.503	0.033	0.049	1.080	3.07	5	Mn	0.5	1319	1319

First crystal phase (main phase): $(\text{K}_a\text{Na}_b\text{Li}_c\text{Ca}_d)_e\text{NbO}_f$

($a+b+c+d=1$, e : an arbitrary value, f : an arbitrary value that constitutes a perovskite structure)

Second crystal phase (secondary phase):

NTK phase: 1115 KTiNbO_5 phase

NTK phase: 1319 KTi_3NbO_9 phase

FIG. 13

Sample	First crystal phase (main phase)								Content of secondary phase (mol%)	Additive metal		Relative dielectric constant ϵ_{33}/ϵ_0	Piezoelectric constant d_{33} (pC/N)	Electro- mechanical coupling factor k_r
	Element C1, C2	a	b	c	d1	d2	e	f		Metal	mol%			
S04 (FIG. 9)	Ca	0.490	0.490	0.020	0	0	1.00	3.00	0	—	0	430	95	0.31
S31 (FIG. 9)	—	0.500	0.500	0.000	0	0	1.00	3.00	0	Cu	1	235	95	0.37
S61	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	5	Zr	1	1207	189	0.42
S62	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	5	Cu, Zr	0.5, 1	1370	224	0.50
S63	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	5	Fe, Zr	0.5, 1	1405	185	0.42
S64	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	5	Zn, Zr	0.5, 1	1414	203	0.46
S65	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	5	Cu, Fe, Zr	0.5, 0.5, 1	1480	234	0.52
S66	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	5	Cu, Fe, Zr	0.6, 0.3, 1	1502	243	0.52
S67	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	5	Fe, Zn, Zr	0.5, 0.5, 1	1445	205	0.47
S68	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	5	Cu, Fe, Zn, Zr	0.5, 0.5, 0.5, 1	1550	253	0.51
S69	Ca	0.449	0.478	0.022	0.050	0	1.08	3.07	5	Cu, Fe, Zr	0.5, 0.5, 1	1390	217	0.48
S70	Ca, Sr	0.449	0.478	0.022	0.039	0.011	1.08	3.07	5	Cu, Fe, Zr	0.5, 0.5, 1	1278	211	0.47
S71	Ca, Ba	0.396	0.532	0.022	0.039	0.011	1.08	3.07	5	Cu, Fe, Zr	0.5, 0.5, 1	1317	205	0.46
S72	Ca	0.396	0.532	0.022	0.050	0	1.08	3.07	5	Ni, Cu, Zr	0.5, 0.5, 1	1329	189	0.43
S73	Ca, Sr	0.396	0.532	0.022	0.039	0.011	1.08	3.07	5	Ni, Cu, Zr	0.5, 0.5, 1	1285	183	0.41
S74	Ca, Ba	0.449	0.478	0.022	0.039	0.012	0.98	3.01	5	Cu, Fe, Zr	0.5, 0.5, 1	904	83	0.24
S75	Ca, Ba	0.449	0.478	0.022	0.039	0.012	1.047	3.05	5	Cu, Fe, Zr	0.5, 0.5, 1	988	121	0.33
S76	Ca	0.396	0.537	0.022	0.045	0	1.08	3.06	5	Ni, Cu, Zr	0.5, 0.5, 1	1070	142	0.37
S77	Ca, Sr	0.396	0.537	0.022	0.034	0.011	1.08	3.06	5	Ni, Cu, Zr	0.5, 0.5, 1	1300	195	0.45
S78	Ca, Ba	0.449	0.478	0.022	0.039	0.011	0.98	3.01	5	Cu, Fe, Zn, Zr	0.5, 0.5, 0.5, 1	1360	174	0.39
S79	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.09	3.07	5	Cu, Fe, Zn, Zr	0.5, 0.5, 0.5, 1	1500	205	0.41
S80	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.12	3.09	5	Cu, Fe, Zn, Zr	0.5, 0.5, 0.5, 1	not closely packed		
S81	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	0	—	0	not closely packed		

First crystal phase (main phase): $(K_aNa_bLi_cCl_dC2_{d2})_eNbO_f$ (C1, C2: at least one of Ca, Sr and Ba, $a+b+c+d1+d2 = 1$, e : an arbitrary value, f : an arbitrary value that constitutes a perovskite structure)Second crystal phase (secondary phase): $K_{0.85}Ti_{0.85}Nb_{1.15}O_5$

FIG. 14

Sample	First crystal phase (main phase)							Content of secondary phase (mol%)	Additive metal		Electromechanical coupling factor k_r		
	Element C1, C2	a	b	c	d1	d2	e	f	Metal	mol%	Initial value	After thermal cycle	Drop rate (%)
S04 (FIG. 9)	Ca	0.490	0.490	0.020	0	0	1.00	3.00	—	0	0.31	0.10	-67.7
S31 (FIG. 9)	—	0.500	0.500	0	0	0	1.00	3.00	Cu	1	0.37	0.12	-67.6
S32 (FIG. 9)	Ca	0.421	0.518	0.022	0.039	0	1.07	3.06	—	0	0.43	0.32	-25.6
S61 (FIG. 13)	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	Zr	1	0.42	0.32	-23.8
S62 (FIG. 13)	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	Cu, Zr	0.5, 1	0.50	0.40	-20.0
S63 (FIG. 13)	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	Fe, Zr	0.5, 1	0.42	0.36	-14.3
S64 (FIG. 13)	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	Zn, Zr	0.5, 1	0.46	0.34	-26.1
S65 (FIG. 13)	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	Cu, Fe, Zr	0.5, 0.5, 1	0.52	0.44	-15.4
S67 (FIG. 13)	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	Fe, Zn, Zr	0.5, 0.5, 1	0.47	0.37	-21.3
S68 (FIG. 13)	Ca, Ba	0.449	0.478	0.022	0.039	0.011	1.08	3.07	Cu, Fe, Zn, Zr	0.5, 0.5, 0.5, 1	0.51	0.45	-11.8
S69 (FIG. 13)	Ca	0.449	0.478	0.022	0.050	0	1.08	3.07	Cu, Fe, Zr	0.5, 0.5, 1	0.48	0.43	-10.4

First crystal phase (main phase): $(K_aNa_bLi_cCl_dC2_{d2})_eNbO_f$

(C1, C2: at least one of Ca, Sr and Ba, $a+b+c+d1+d2=1$, e : an arbitrary value, f : an arbitrary value that constitutes a perovskite structure)

Second crystal phase (secondary phase): $K_{0.85}Ti_{0.85}Nb_{1.15}O_5$

Test method

- (1) Place a piezoelectric element in a thermostat and evaluate the piezoelectric properties of the piezoelectric element at room temperature (as the initial properties of the piezoelectric element).
- (2) Subject the piezoelectric element to thermal cycle of -50°C, 150°C, 20°C, 150°C and 20°C at a temperature increase/decrease rate of 2°C/min (holding time: 1 hour at each temperature).
- (3) Evaluate the piezoelectric properties of the piezoelectric element at room temperature (as the properties of the piezoelectric element after the thermal cycle).

