

FIG. 1

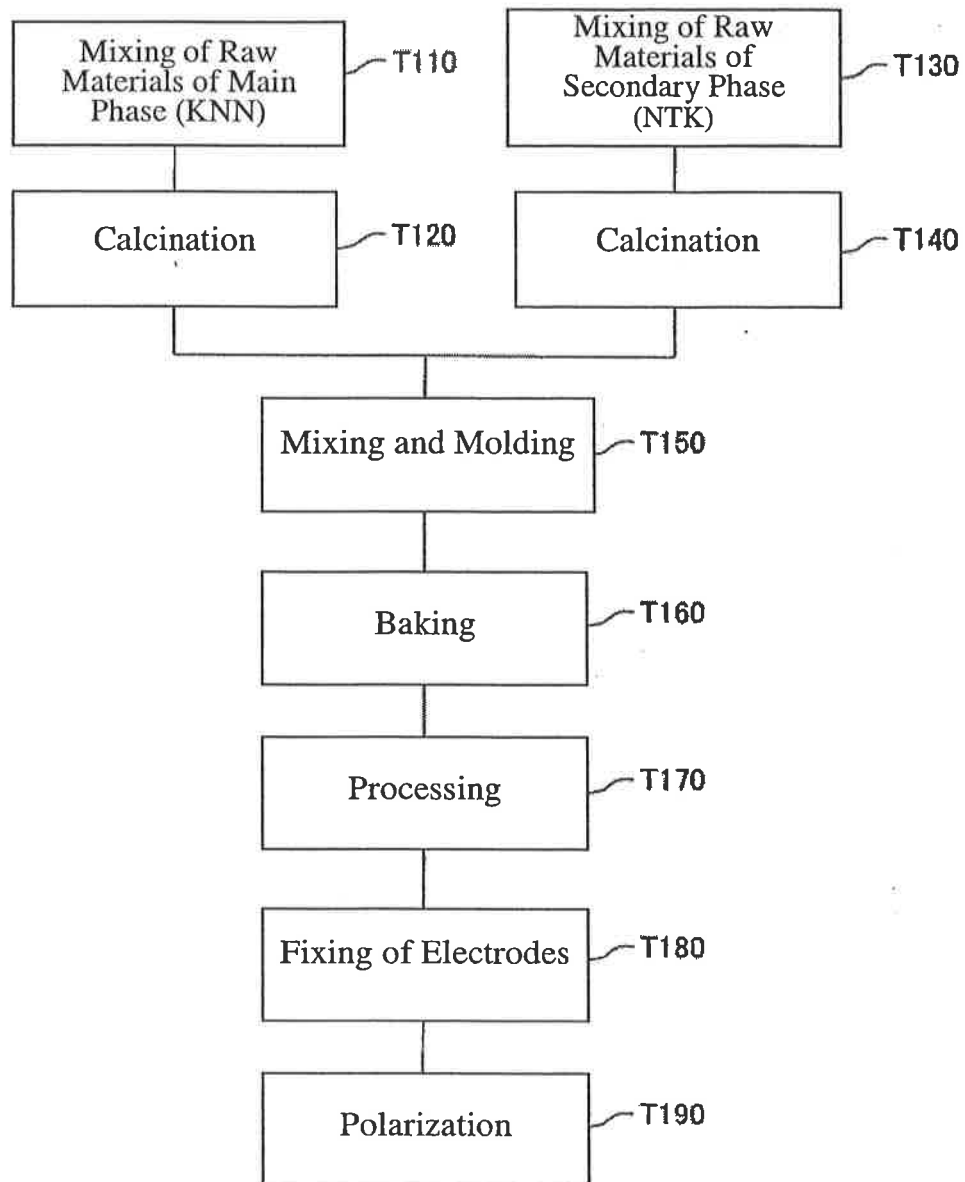


FIG. 2

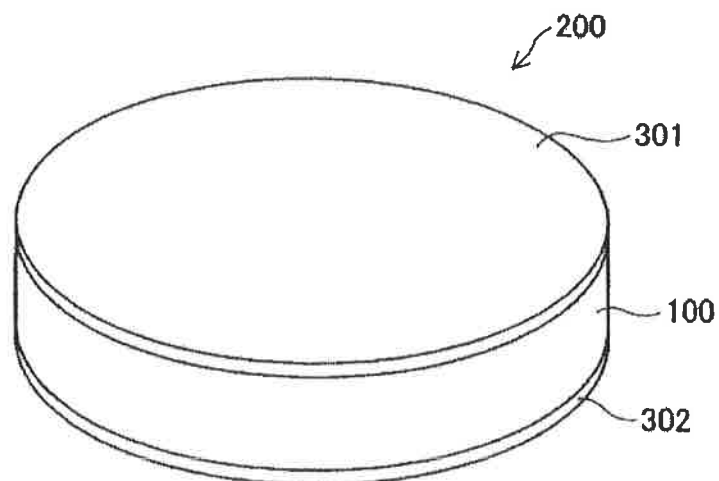


FIG. 3A

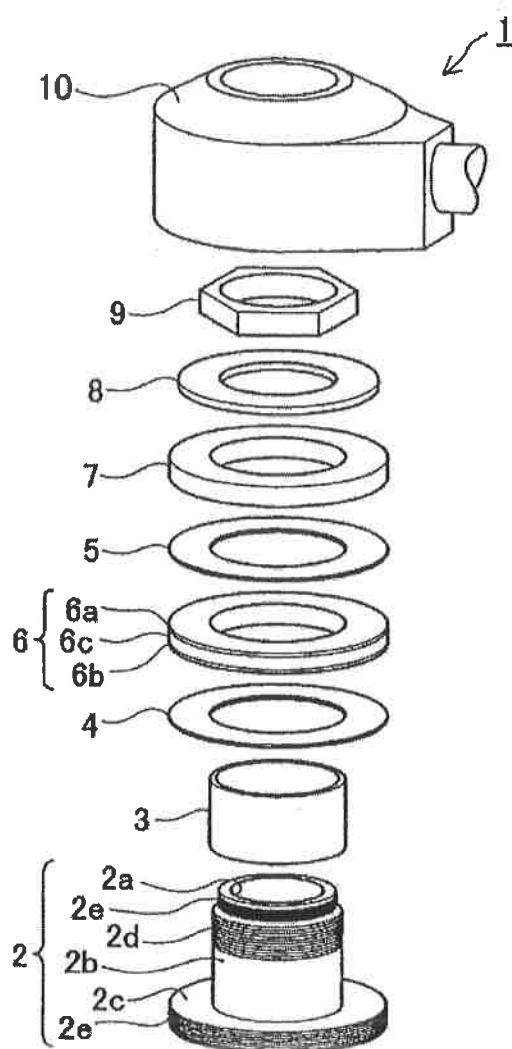


FIG. 3B

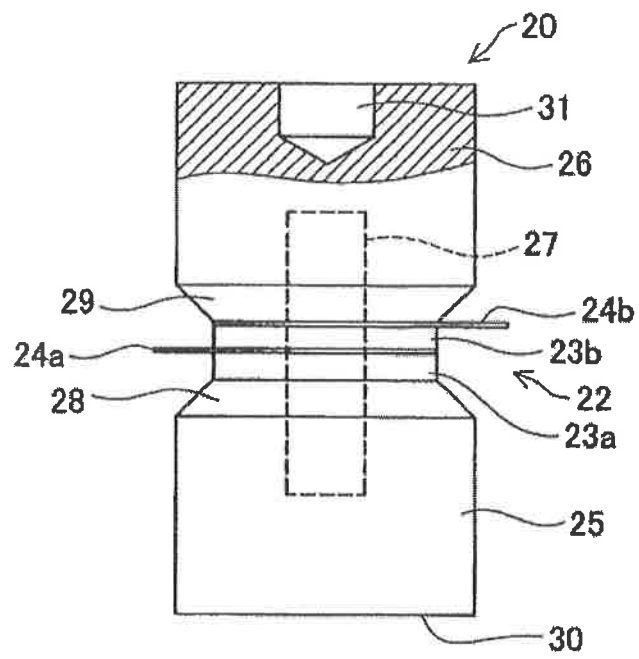


FIG. 3C

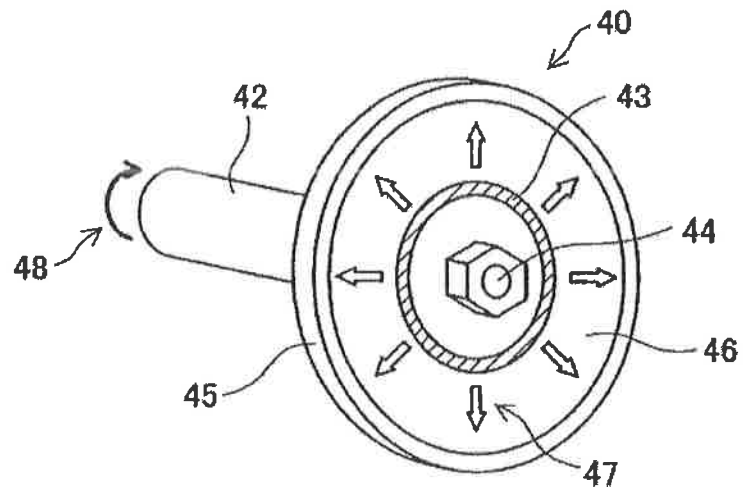


FIG. 4

| Sample | First crystal phase<br>(main phase) |              |       |       |       |       | Second crystal phase<br>(secondary phase) |      |              | Content of<br>secondary<br>phase<br>(mol%) | Relative<br>dielectric<br>constant<br>$\epsilon_{33}^T/\epsilon_0$ | Piezoelectric<br>constant<br>$d_{33}$ (pC/N) | Electro-<br>mechanical<br>coupling<br>factor $k_r$ |
|--------|-------------------------------------|--------------|-------|-------|-------|-------|-------------------------------------------|------|--------------|--------------------------------------------|--------------------------------------------------------------------|----------------------------------------------|----------------------------------------------------|
|        | Element<br>C                        | Element<br>B | a     | b     | c     | d     | e                                         | f    | Element<br>A | Element<br>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):  $(K_aNa_bLi_cCa_d)_eDO_f$

(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

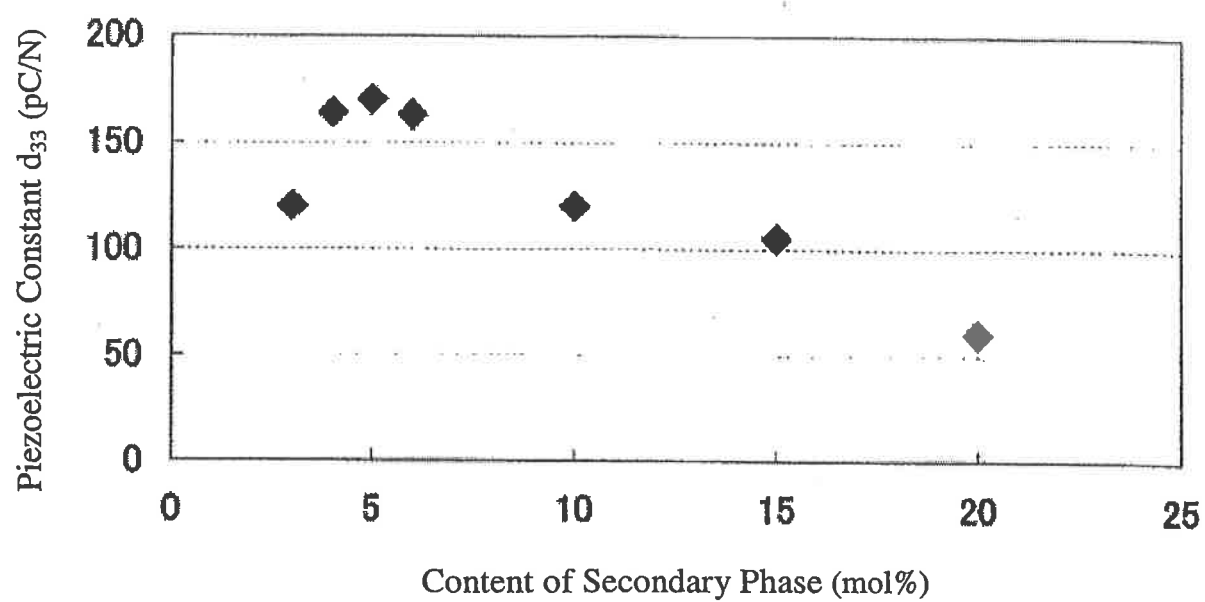


FIG. 6

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

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

(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<br>(main phase) |       |       |       |       | Second crystal phase<br>(secondary phase) |              |              | Content of<br>secondary<br>phase<br>(mol%) | Relative<br>dielectric<br>constant<br>$\epsilon_{33}^T/\epsilon_0$ | Piezoelectric<br>constant<br>$d_{33}$ (pC/N) | Electro-<br>mechanical<br>coupling<br>factor $k_r$ |
|-----------|-------------------------------------|-------|-------|-------|-------|-------------------------------------------|--------------|--------------|--------------------------------------------|--------------------------------------------------------------------|----------------------------------------------|----------------------------------------------------|
|           | $a$                                 | $b$   | $c$   | $d$   | $e$   | $f$                                       | Element<br>A | Element<br>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):  $(K_aNa_bLi_cCa_d)_2NbO_f$

( $a+b+c+d=1$ ,  $e$ : 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

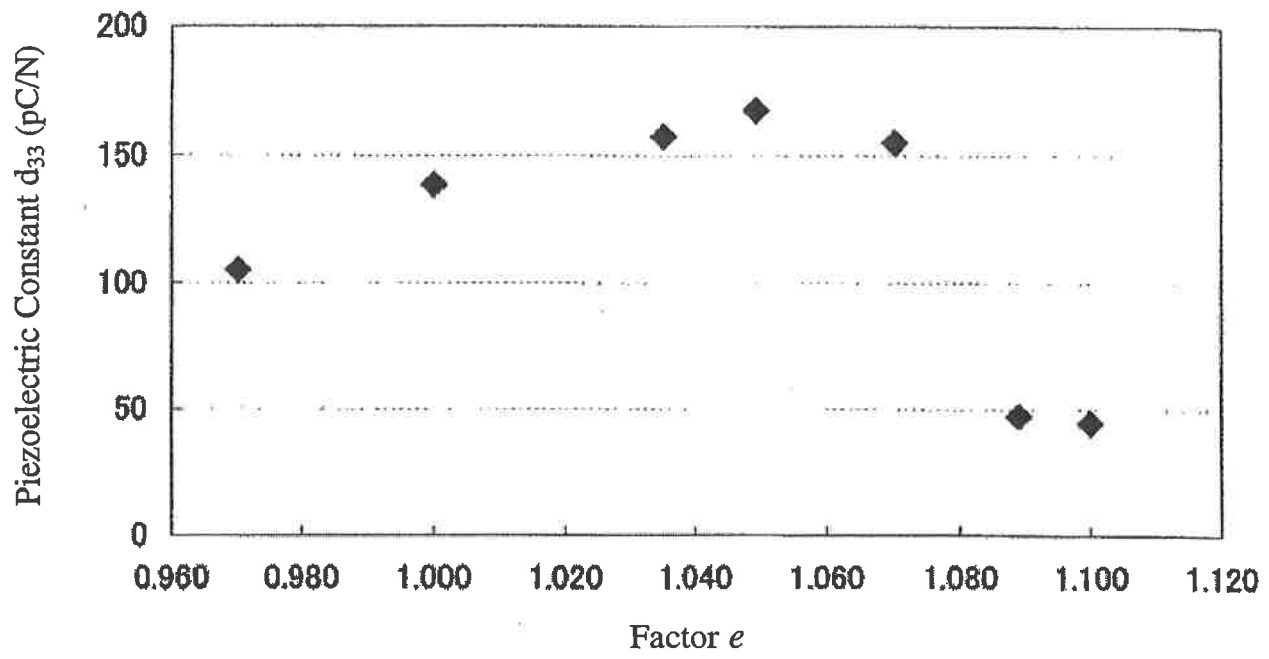


FIG. 9

| Sample    | First crystal phase<br>(main phase) |       |       |       |       | Second crystal phase<br>(secondary phase) |              |              | Content of<br>secondary<br>phase<br>(mol%) | Additive metal |            | Relative<br>dielectric<br>constant<br>$\epsilon_{33}^T/\epsilon_0$ | Piezoelectric<br>constant<br>$d_{33}$ (pC/N) | Electro-<br>mechanical<br>coupling<br>factor $k_r$ |
|-----------|-------------------------------------|-------|-------|-------|-------|-------------------------------------------|--------------|--------------|--------------------------------------------|----------------|------------|--------------------------------------------------------------------|----------------------------------------------|----------------------------------------------------|
|           | $a$                                 | $b$   | $c$   | $d$   | $e$   | $f$                                       | Element<br>A | Element<br>B |                                            | 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           | 5                                          | —              | 0          | 1130                                                               | 170                                          | 0.43                                               |
| S33       | 0.455                               | 0.484 | 0.022 | 0.039 | 1.070 | 3.06                                      | K            | Nb           | 5                                          | Cu             | 0.5        | 1050                                                               | 186                                          | 0.46                                               |
| S34       | 0.455                               | 0.484 | 0.022 | 0.039 | 1.070 | 3.06                                      | K            | Nb           | 5                                          | Cu             | 1          | 985                                                                | 138                                          | 0.38                                               |
| S35       | 0.455                               | 0.484 | 0.022 | 0.039 | 1.070 | 3.06                                      | K            | Nb           | 5                                          | Cu<br>Fe       | 0.5<br>0.5 | 1042                                                               | 200                                          | 0.48                                               |
| S36       | 0.464                               | 0.474 | 0.022 | 0.039 | 1.070 | 3.06                                      | K            | Nb           | 5                                          | Fe             | 0.5        | 1119                                                               | 199                                          | 0.48                                               |
| S37       | 0.464                               | 0.474 | 0.022 | 0.039 | 1.070 | 3.06                                      | K            | Nb           | 5                                          | Cu<br>Ni       | 0.5<br>0.5 | 1150                                                               | 170                                          | 0.44                                               |
| S38       | 0.464                               | 0.474 | 0.022 | 0.039 | 1.070 | 3.06                                      | K            | Nb           | 5                                          | Ag             | 0.5        | 1060                                                               | 171                                          | 0.42                                               |
| S39       | 0.464                               | 0.474 | 0.022 | 0.039 | 1.070 | 3.06                                      | K            | Nb           | 5                                          | Zr             | 0.5        | 1121                                                               | 166                                          | 0.42                                               |
| S40       | 0.464                               | 0.474 | 0.022 | 0.039 | 1.070 | 3.06                                      | K            | Nb           | 5                                          | Zn             | 0.5        | 1221                                                               | 175                                          | 0.42                                               |
| S41       | 0.464                               | 0.474 | 0.022 | 0.039 | 1.070 | 3.06                                      | K            | Nb           | 5                                          | Sc<br>Bi       | 0.5<br>0.5 | 1213                                                               | 172                                          | 0.41                                               |
| S42       | 0.464                               | 0.474 | 0.022 | 0.039 | 1.070 | 3.06                                      | K            | Nb           | 5                                          | Mn             | 0.5        | 976                                                                | 156                                          | 0.42                                               |
| S43       | 0.455                               | 0.474 | 0.022 | 0.049 | 1.070 | 3.06                                      | K            | Nb           | 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<br>(main phase) |          |          |          |          | Second crystal phase<br>(secondary phase) |              |              | Content of<br>secondary<br>phase<br>(mol%) | Additive metal |          | Applicable<br>voltage <sup>cf.)</sup><br>(kV/mm) |
|--------|-------------------------------------|----------|----------|----------|----------|-------------------------------------------|--------------|--------------|--------------------------------------------|----------------|----------|--------------------------------------------------|
|        | <i>a</i>                            | <i>b</i> | <i>c</i> | <i>d</i> | <i>e</i> | <i>f</i>                                  | Element<br>A | Element<br>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):  $(K_aNa_bLi_cCa_d)_2NbO_f$   
 $(a+b+c+d = 1, e: \text{an arbitrary value}, f: \text{an arbitrary value that constitutes a perovskite structure})$

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  $\text{KTiNbO}_5$  phase as second crystal phase

| Sample       | First crystal phase<br>(main phase) |       |       |       |       |      | Content of<br>secondary<br>phase<br>(mol%) | Additive metal |          | NTK phase<br>(XRD) | NTK phase<br>(TEM-EDS) |
|--------------|-------------------------------------|-------|-------|-------|-------|------|--------------------------------------------|----------------|----------|--------------------|------------------------|
|              | a                                   | b     | c     | d     | e     | f    |                                            | 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):  $(\text{K}_a\text{Na}_b\text{Li}_c\text{Ca}_d)_2\text{NbO}_f$

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

Second crystal phase (secondary phase):

NTK phase: 1115  $\text{KTiNbO}_5$  phase

NTK phase: 1319  $\text{KTi}_3\text{NbO}_9$  phase

FIG. 12

The case of mixing  $\text{KTi}_3\text{NbO}_9$  phase as second crystal phase

| Sample | First crystal phase<br>(main phase) |          |          |          |          | Content of<br>secondary<br>phase<br>(mol%) | Additive metal |          | NTK phase<br>(XRD) | NTK phase<br>(TEM-EDS) |
|--------|-------------------------------------|----------|----------|----------|----------|--------------------------------------------|----------------|----------|--------------------|------------------------|
|        | <i>a</i>                            | <i>b</i> | <i>c</i> | <i>d</i> | <i>e</i> |                                            | Metal          | mol%     |                    |                        |
| S51    | 0.421                               | 0.518    | 0.022    | 0.039    | 1.070    | 3                                          | —              | 0        | —                  | 1319                   |
| S52    | 0.421                               | 0.518    | 0.022    | 0.039    | 1.070    | 5                                          | —              | 0        | 1319               | 1319                   |
| S53    | 0.455                               | 0.484    | 0.022    | 0.039    | 1.070    | 5                                          | Cu             | 0.5      | —                  | 1319                   |
| S54    | 0.455                               | 0.484    | 0.022    | 0.039    | 1.070    | 5                                          | Cu, Fe         | 0.5, 0.5 | 1319               | 1319                   |
| S55    | 0.421                               | 0.518    | 0.022    | 0.039    | 1.070    | 5                                          | Fe             | 0.5      | 1319               | 1319                   |
| S56    | 0.421                               | 0.508    | 0.022    | 0.049    | 1.070    | 5                                          | Zn             | 0.5      | 1319               | 1319                   |
| S57    | 0.416                               | 0.503    | 0.033    | 0.049    | 1.080    | 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  $\text{KTiNbO}_5$  phase

NTK phase: 1319  $\text{KTi}_3\text{NbO}_9$  phase

FIG. 13

| Sample       | First crystal phase<br>(main phase) |       |       |       |       |       |       | Content of<br>secondary<br>phase<br>(mol%) | Additive metal |                | Relative<br>dielectric<br>constant<br>$\epsilon_{33}^T/\epsilon_0$ | Piezoelectric<br>constant<br>$d_{33}$ (pC/N) | Electro-<br>mechanical<br>coupling<br>factor $k_r$ |      |
|--------------|-------------------------------------|-------|-------|-------|-------|-------|-------|--------------------------------------------|----------------|----------------|--------------------------------------------------------------------|----------------------------------------------|----------------------------------------------------|------|
|              | Element<br>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<br>(main phase) |       |       |       |       |       |      | Content of<br>secondary<br>phase<br>(mol%) | Additive metal |                  | Electromechanical<br>coupling factor $k_r$ |                           |                     |
|---------------|-------------------------------------|-------|-------|-------|-------|-------|------|--------------------------------------------|----------------|------------------|--------------------------------------------|---------------------------|---------------------|
|               | Element<br>C1, C2                   | a     | b     | c     | d1    | d2    | e    | f                                          | Metal          | mol%             | Initial<br>value                           | After<br>thermal<br>cycle | Drop<br>rate<br>(%) |
| 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).

