

## Dielectric and Piezoelectric Properties of “Lead-free” Piezoelectric Rhombohedral $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$ Single Crystals

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### ABSTRACT

Rhombohedral  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals are fabricated using the cost-effective solid-state single crystal growth (SSCG) method; their dielectric and piezoelectric properties are also characterized. Measurements show that (001)  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals have an electromechanical coupling factor ( $k_{33}$ ) higher than 0.85, piezoelectric charge constant ( $d_{33}$ ) of about 950 [pC/N], and piezoelectric voltage constant ( $g_{33}$ ) higher than 40 [ $\times 10^{-3}$  Vm/N]. Especially the  $d_{33}$  of (001)  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals was by about six times higher than that of their ceramics. Because their electromechanical coupling factor ( $k_{33}$ ) and piezoelectric voltage constant ( $d_{33}$ ,  $g_{33}$ ) are higher than those of soft PZT ceramics, it is expected that rhombohedral (001)  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals can be used as “lead-free” piezoelectric materials in many piezoelectric applications such as actuator, sensor, and transducer.

**Key words :** Piezoelectric, Lead-free, Single Crystals,  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$

### 1. Introduction

**P** $\text{b}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) -based polycrystalline ceramics have been used mainly for diversified piezoelectric applications up to now.<sup>1)</sup> They have been used in various ways for not only civilian application areas such as piezoelectric ignition device, ultrasonic motor, piezoelectric speaker, piezoelectric sensor, piezoelectric actuator, piezoelectric transformer and medical ultrasonic diagnostic instruments, etc. but also military application areas such as SONAR. However, as interests on environmental problems due to the hazards of lead(Pb) contained in piezoelectric PZT ceramics are increased recently, development of lead-free piezoelectric materials capable of replacing the PZT ceramics has been actively implemented by Japan, Europe and Korea at the center.<sup>2-4)</sup>

The lead-free piezoelectric ceramics developed thus far to replace PZT ceramics include tungsten-bronze structure, bismuth layer structure and perovskite structure, etc. However, the lead-free piezoelectric ceramics developed are known to have a difficulty in replacing the PZT ceramics yet due to the lower dielectric and piezoelectric properties compared with those of general PZT ceramics or a difficulty in mass production processes. Recently, to overcome the low dielectric and piezoelectric properties of lead-free piezoelectric ceramics, attempts have been made to replace PZT

ceramics by development of high-performance textured ceramics or single crystals. As revealed by many previous study results on linked PMN-PT single crystals,<sup>5-7)</sup> lead-free textured ceramics or single crystals are expected to show very high piezoelectric constants and electromechanical coupling factors compared with general polycrystalline piezoelectric ceramics composed of randomly oriented grains. And, recently-developed lead-free KNN-based single crystals were reported to show a high electromechanical coupling factor ( $k_{33}$ ) higher than 0.8 as had been expected.<sup>8-10)</sup> Since, however, single-crystal piezoelectric materials such as KNN series, etc. have prices which are a few to a few ten times as high as those of general polycrystalline PZT ceramics due to a difficulty in single crystal manufacturing, replacement of polycrystalline piezoelectric materials remains to be difficult. Therefore, to replace the PZT ceramics, development of a technology capable of mass-producing high-performance lead-free piezoelectric single crystals at a low manufacturing cost is required.

In the present study,  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals were selected as a lead-free piezoelectric single crystal, and development of high-efficiency lead-free piezoelectric single crystals was attempted by using solid-state single crystal growth [SSCG] method.<sup>7,11)</sup> Since  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  compositions showing incongruent melting behavior are difficult to manufacture by general single crystal growth methods such as flux method or Bridgman method, etc. solid-state single crystal growth method was employed without including a melting process upon growth of single crystals. And, the solid-state single-crystal growth method is known to have a low cost for single-crystal manufacturing, and to allow mass

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production. Dielectric and piezoelectric properties of the grown  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals were measured and evaluated,<sup>6,7,12)</sup> and compared with those for the existing piezoelectric PZT polycrystalline ceramics. Through the present study, excellent dielectric and piezoelectric properties of  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystal have been affirmed, and the future possibility of its use as a high-performance lead-free piezoelectric material has been demonstrated.

## 2. Experimental Procedure

Lead-free piezoelectric  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals used in the present study were prepared by using solid-state single-crystal growth (SSCG) method. First, by using raw material powders of  $\text{BaCO}_3$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$ , polycrystalline  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  ceramics were obtained through a general sintering process. After weighing each raw material powder for  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  composition, they were mixed for 24 h using ball-milling process, and calcined at  $1,000^\circ\text{C}$  following drying. The calcined powders were subjected to the second ball-milling, forming under uniaxial compression following drying, and then sintered. After the first sintering, a  $\text{BaTiO}_3$  seed single crystal was placed on the sintered body of  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$ , and the second heat treatment for solid-state single-crystal growth was carried out for 100 hours.

The  $\text{BaTiO}_3$  seed single crystal was continuously grown into the  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  polycrystalline body during the heat treatment process for single-crystal growth, and  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals of a size larger than  $25 \times 25 \times 5 \text{ mm}^3$  were prepared as a result. Since no melting in  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  occurred during single-crystal manufacturing process in the single-crystal growth method, composition gradients were not observed within the grown single crystal, giving rise to a chemical homogeneity. Thus prepared single crystals larger than  $25 \times 25 \times 5 \text{ mm}^3$  in size were cut into a plate shape (specimen of  $[3 \times 3 \times 0.5(\text{t}) \text{ m}^3]$  for thickness mode measurement) and a square-column shape (specimen of  $[1 \times 1 \times 5(\text{t}) \text{ m}^3]$  for 33 mode measurement) single-crystal specimens, and an Au electrode was formed on the cut single-crystal plate by using vacuum deposition method. Dielectric and piezoelectric properties of the manufactured  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals and polycrystalline ceramics were measured in accordance with the IEEE standard.<sup>12)</sup> And (001) single crystals and (011) single crystals were produced respectively for observation of property changes in the single crystals as a function of crystal orientation.

## 3. Results and Discussion

### 3.1 $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$ single crystals prepared by solid-state single-crystal growth method

Figure 1 shows a  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystal prepared by the solid-state single-crystal growth method. A  $\text{BaTiO}_3$  seed single crystal is positioned at the center part of the specimen, and the  $\text{BaTiO}_3$  seed single crystal was continu-

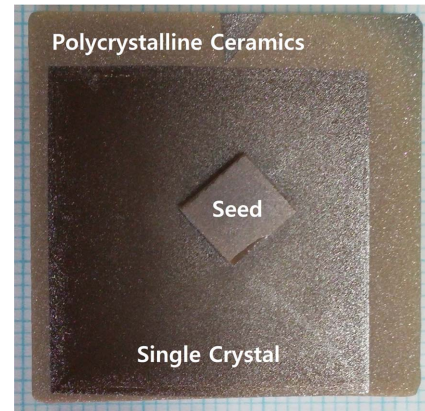


Fig. 1. A (001)  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystal grown by the SSCG method.

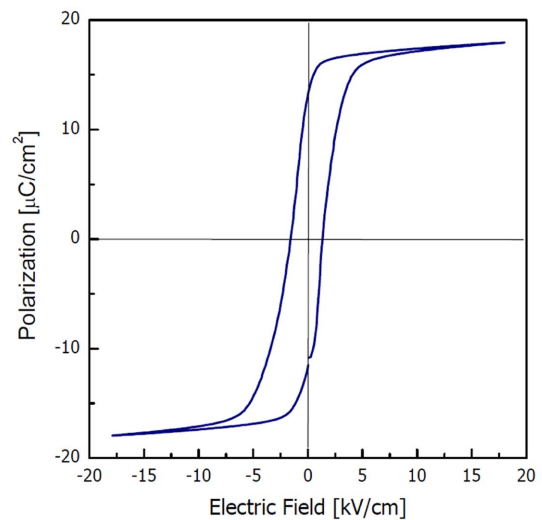


Fig. 2. Polarization of a rhombohedral (001)  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystal plate [ $4 \times 4 \times 0.5(\text{t}) \text{ mm}^3$ ] as a function of electric field.

ously grown into the  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  polycrystalline body during the heat treatment process for single-crystal growth. After heat treatment process,  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals larger than  $25 \times 25 \times 5 \text{ mm}^3$  in size were manufactured inside the  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  polycrystalline body. Since single-crystal growth in the solid-state single crystal growth method occurs at a temperature below the melting point for the  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  phase, the shape of polycrystalline  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  ceramics around the grown  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystal was maintained. And, no composition gradients were observed in the manufactured  $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$  single crystals and polycrystalline bodies with a chemical homogeneity being obtained even after the heat treatment process for single crystal growth.

### 3.2 Polarization properties of rhombohedral (001) $\text{Ba}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$ single crystal

In Fig. 2, variations in polarization properties as a function of electric field variation were observed by using a

plate-shaped (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal[4 × 4 × 0.5(t) mm<sup>3</sup>]. In Fig. 2, the value of saturated polarization (P<sub>s</sub>) was shown to be about 28.8 [μC/cm<sup>2</sup>], and remanent polarization (P<sub>r</sub>) was observed to be about 12.5 [μC/cm<sup>2</sup>]. In addition, coercive electric field (E<sub>c</sub>) was measured to be about 1.5 kV/cm.

**3.3. Dielectric and piezoelectric properties of rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal**

In Table 1, dielectric and piezoelectric property values of plate-shaped rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals and polycrystalline ceramics are arranged. According to Table 1(a) for rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals, dielectric constant(K<sub>3<sup>T</sup></sub>) was measured to be higher than 2,000, dielectric loss (tan δ, %) about 0.4, and piezoelectric charge constant (d<sub>33</sub>) about 950 [pC/N]. In Table 1(b) for Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> polycrystalline ceramics, dielectric constant (K<sub>3<sup>T</sup></sub>) was measured to be higher than 1,230, dielectric loss (tan δ, %) about 3.7, and piezoelectric charge constant (d<sub>33</sub>) about 165 [pC/N]. As compared with

the polycrystalline ceramics, the (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal had a piezoelectric charge constant higher by more than 6 times and a dielectric loss smaller by more than 9 times.

In Table 2, dielectric and piezoelectric properties in 33 mode were measured by using rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals of a square column form [1 × 1 × 5(t) mm<sup>3</sup>]. According to Table 2 for (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals, electromechanical coupling factor (k<sub>33</sub>) was measured to be 0.85, piezoelectric charge constant (d<sub>33</sub>) about 950 [pC/N], piezoelectric voltage constant (g<sub>33</sub>) about 41 [x10<sup>-3</sup> Vm/N], and elastic compliance (s<sub>33<sup>E</sup></sub>) about 39.2 [x 10<sup>-12</sup> m<sup>2</sup>/N]. Such high electromechanical coupling factor (k<sub>33</sub>) and piezoelectric constants (d<sub>33</sub>, g<sub>33</sub>) of such rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals showed higher values than those of general polycrystalline PZT ceramics. Therefore, rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals exhibited the possibility for replacement of the linked piezoelectric PZT ceramics in diversified piezo-

**Table 1.** Dielectric and Piezoelectric Properties of (a) (001) Single Crystals and (b) Rhombohedral Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> Polycrystalline Ceramics at Room Temperature

(a) (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal plates [3 × 3 × 0.5(t) m<sup>3</sup>]

Thickness Mode		[001] Ba(Ti <sub>0.92</sub> Zr <sub>0.08</sub> )O <sub>3</sub> Single Crystal Plates- Poled along the [001] axis				
		11	12	13	Average	STDEV.
Thickness	mm	0.50	0.50	0.50	<b>0.50</b>	0.00
Width	mm	3.00	3.00	3.00	<b>3.0</b>	0.00
Length	mm	3.00	3.00	3.00	<b>3.0</b>	0.00
Density	g/cm <sup>3</sup>	5.60	5.60	5.60	<b>5.6</b>	0.00
Capacitance	nF	0.330	0.323	0.331	<b>0.328</b>	0.004
tan δ	/	0.003	0.003	0.005	<b>0.004</b>	0.001
f <sub>r</sub>	kHz	4,404.6	4,374.0	4,374.0	<b>4,384.2</b>	17.7
f <sub>a</sub>	kHz	5,170.0	5,466.3	5,562.4	<b>5,399.6</b>	204.5
Z <sub>r</sub>	kOhm	0.02	0.02	0.02	<b>0.02</b>	0.00
K <sub>3<sup>T</sup></sub>	/	<b>2,072</b>	<b>2,028</b>	<b>2,079</b>	<b>2,060</b>	27
k <sub>t</sub>	/	<b>0.563</b>	<b>0.639</b>	<b>0.656</b>	<b>0.62</b>	0.05
d <sub>33</sub>	pC/N	944	926	961	<b>943.7</b>	17.5

(b) Polycrystalline Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> ceramic plates [3 × 3 × 0.5(t) m<sup>3</sup>]

Thickness Mode		Ba(Ti <sub>0.92</sub> Zr <sub>0.08</sub> )O <sub>3</sub> Ceramic Plates				
		11	12	13	Average	STDEV.
Thickness	mm	0.50	0.50	0.50	<b>0.50</b>	0.00
Width	mm	3.00	3.00	3.00	<b>3.0</b>	0.00
Length	mm	3.00	3.00	3.00	<b>3.0</b>	0.00
Density	g/cm <sup>3</sup>	5.60	5.60	5.60	<b>5.6</b>	0.00
Capacitance	nF	0.190	0.200	0.198	<b>0.196</b>	0.005
tan δ	/	0.034	0.041	0.036	<b>0.037</b>	0.004
f <sub>r</sub>	kHz	4,872.8	4,872.8	4,722.4	<b>4,822.6</b>	86.8
f <sub>a</sub>	kHz	5,260.8	5,242.6	5,224.3	<b>5,242.6</b>	18.3
Z <sub>r</sub>	kOhm	0.06	0.06	0.07	<b>0.06</b>	0.01
K <sub>3<sup>T</sup></sub>	/	<b>1,193</b>	<b>1,257</b>	<b>1,241</b>	<b>1,230</b>	33
k <sub>t</sub>	/	<b>0.412</b>	<b>0.403</b>	<b>0.465</b>	<b>0.43</b>	0.03
d <sub>33</sub>	pC/N	<b>154</b>	<b>162</b>	<b>177</b>	<b>164.3</b>	11.7

**Table 2.** Dielectric and Piezoelectric Properties of Rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> Single Crystal Bars [1 × 1 × 5(t) mm<sup>3</sup>] at Room Temperature

k <sub>33</sub> Mode (LE)		[001] Ba(Ti <sub>0.92</sub> Zr <sub>0.08</sub> )O <sub>3</sub> Single Crystal Bars - Poled along the [001] axis				
		11	12	13	Average	STDEV.
Thickness	mm	5.00	5.00	5.00	5.00	0.00
Width	mm	1.00	1.00	1.00	1.0	0.00
Length	mm	1.00	1.00	1.00	1.0	0.00
Density	g/cm <sup>3</sup>	5.60	5.60	5.60	5.6	0.00
Capacitance	nF	0.003	0.004	0.003	0.003	0.000
tan d	/	0.008	0.001	0.004	0.004	0.004
f <sub>r</sub>	kHz	229.55	226.69	230.99	229.08	2.19
f <sub>a</sub>	kHz	405.91	418.82	400.86	408.53	9.27
Z <sub>r</sub>	kOhm	2.89	2.51	3.19	2.86	0.34
K <sub>3</sub> <sup>T</sup>	/	1,852	2,005	1,804	1,887	105
k <sub>33</sub>	/	0.850	0.864	0.843	0.85	0.01
g <sub>33</sub>	x10 <sup>-3</sup> V m/N	41	41	41	41	0
s <sub>33</sub> <sup>D</sup>	x10 <sup>-12</sup> m <sup>2</sup> /N	10.8	10.2	11.1	10.7	0.5
s <sub>33</sub> <sup>E</sup>	x10 <sup>-12</sup> m <sup>2</sup> /N	39.0	40.2	38.4	39.2	0.9
Y <sub>33</sub>	GPa	25.7	24.9	26.0	25.5	0.6
N <sub>33</sub>	Hz · m	1148	1133	1155	1145	10.9
d <sub>33</sub> [d <sub>33</sub> meter]	pC/N	1,010	951	902	954	54

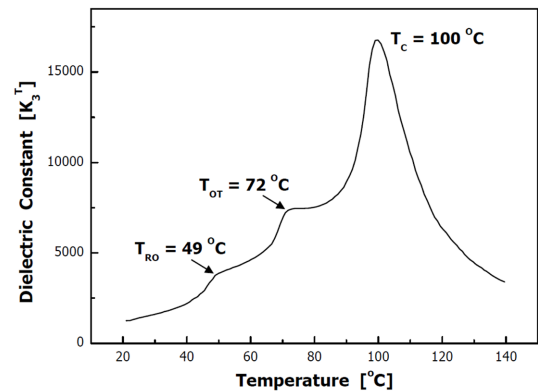
electric applications.

### 3.4 Variations in dielectric and piezoelectric properties as a function of temperatures of rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal

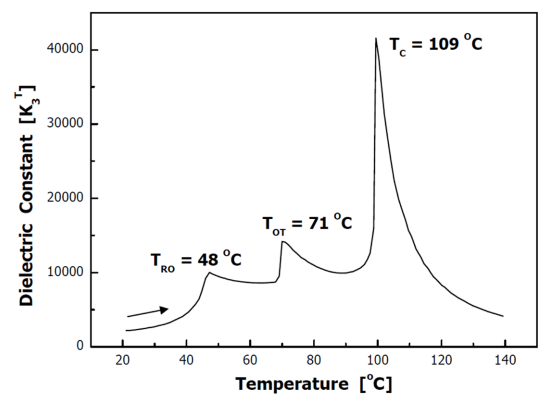
Figure 3 shows variations in dielectric constant for a rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal as a function of temperature variation. As shown in Fig. 3(a) for an unpoled (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal, the phase transition temperature between rhombohedral and orthorhombic phases (T<sub>RO</sub>), that between orthorhombic and tetragonal phases (T<sub>OT</sub>), and that between tetragonal and cubic phases (T<sub>C</sub>) were observed to be 49, 72, and 100°C, respectively. And, T<sub>RO</sub>, T<sub>OT</sub> and T<sub>C</sub> for a poled (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal [Fig. 3(b)] were observed to be 48, 71, and 109°C, respectively.

As compared with the unpoled single crystal [Fig. 3(a)], the poled (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal [Fig. 3(b)] had similar T<sub>RO</sub> and T<sub>OT</sub> but higher T<sub>C</sub> by about 9°C. And, the (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal [Fig. 3(b)] had a dielectric constant higher by more than twice than the unpoled single crystal [Fig. 3(a)] at each phase transition temperature.

Figure 4 shows variations in piezoelectric charge constant (d<sub>33</sub>) of a rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal as a function of temperature variation. When the rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal was heated from room temperature, piezoelectric charge constant (d<sub>33</sub>) was continuously increased to reach a maximum near each phase transition temperature [T<sub>RO</sub>, T<sub>OT</sub> and T<sub>C</sub>]. And, when



(a) Unpoled (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal

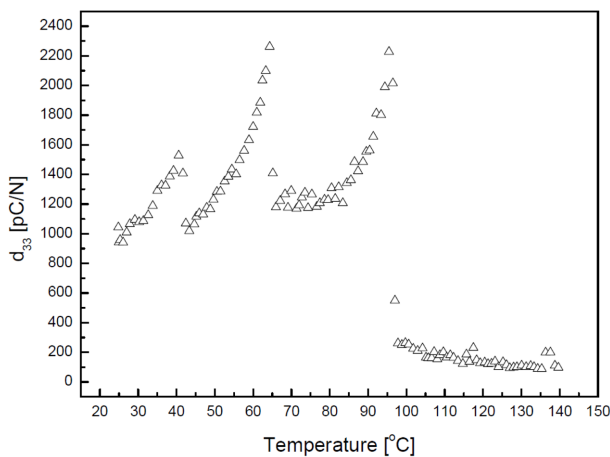


(b) Poled (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal

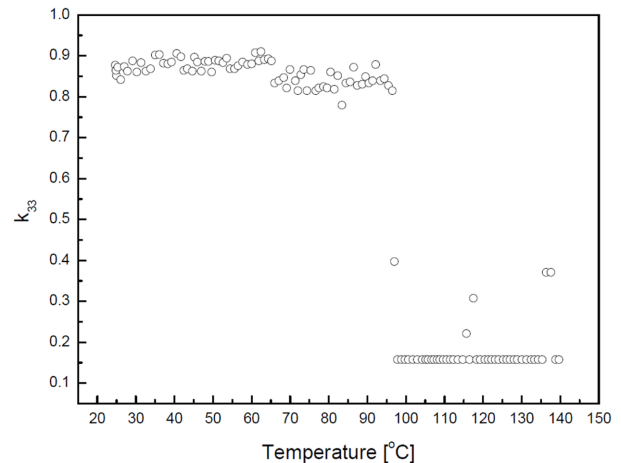
**Fig. 3.** Dielectric constants of (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal plates [4 × 4 × 0.5(t) mm<sup>3</sup>] as a function of temperature: (a) unpoled and (b) poled.

the phase transition temperature was exceeded on the basis of each phase transition temperature [ $T_{RO}$ ,  $T_{OT}$  and  $T_C$ ] as shown in Fig. 4, piezoelectric charge constant ( $d_{33}$ ) was sharply reduced and then continuously increased as the temperature was raised. And, above  $T_C$ , the piezoelectric charge constant ( $d_{33}$ ) was drastically reduced. Thus, as the piezoelectric charge constant ( $d_{33}$ ) became a maximum near each phase transition temperature [ $T_{RO}$ ,  $T_{OT}$  and  $T_C$ ] with an increase in temperatures, the spontaneous polarization direction is discontinuously changed with a drastic reduction in the piezoelectric charge constant. Such phenomenon is well known in the previous studies on BaTiO<sub>3</sub> and PMN-PT piezoelectric single crystals.<sup>5-7,11</sup> Also, with the phase transition from tetragonal phase to non-ferroelectric cubic phase near 109°C, the piezoelectric charge constant ( $d_{33}$ ) was drastically reduced to less than 100 [pC/N]. Variations in piezoelectric charge constant ( $d_{33}$ ) for a rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal as a function of temperature in Fig. 4 show the results in agreement with behavior of dielectric property variations for a rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal as a function of temperature variation in Fig. 3.

Figure 5 shows variations in electromechanical coupling factor ( $k_{33}$ ) for a rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal as a function of temperature variation. When a rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal was heated from room temperature, the electromechanical coupling factor ( $k_{33}$ ) exhibited a uniform value within the range of  $\pm 10\%$  below  $T_C$  as shown in Fig. 5. Namely, unlike dielectric constant (Fig. 3) and piezoelectric constant (Fig. 4), the phenomenon was not observed where a maximum value occurred near each phase transition temperature [ $T_{RO}$ ,  $T_{OT}$  and  $T_C$ ] with a drastic reduction again when the phase transition temperature was exceeded. Such behavior differed from the previous study results on BaTiO<sub>3</sub> and PMN-PT piezoelectric single crystals where the electromechanical coupling factor ( $k_{33}$ ) was reported to show a maximum value



**Fig. 4.** Piezoelectric constant ( $d_{33}$  [pC/N]) of a (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal bar [ $1 \times 1 \times 5(t)$  mm<sup>3</sup>] as a function of temperature.



**Fig. 5.** Electromechanical coupling factor ( $k_{33}$ ) of a (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal bar [ $1 \times 1 \times 5(t)$  mm<sup>3</sup>] as a function of temperature.

at each phase transition temperature.<sup>5-7,11</sup> The electromechanical coupling factor ( $k_{33}$ ) shows a tendency of being proportional to the piezoelectric constant squared and inversely proportional to the dielectric constant [ $k_{33} = d_{33}^2 / s_{33}^E \epsilon_r$ ]. Therefore, the fact that the electromechanical coupling factor ( $k_{33}$ ) for a rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal did not show a drastic change near each phase transition temperature [ $T_{RO}$ ,  $T_{OT}$  and  $T_C$ ] seems to suggest that an increase in the piezoelectric constant and an increase in the product between elastic compliance [ $s_{33}^E$ ] and dielectric constant [ $\epsilon_r$ ] were shown to be offset. Due to such offset phenomenon, relatively uniform values are considered to have been observed without showing a drastic change in the electromechanical coupling factor ( $k_{33}$ ) near each phase transition temperature.

### 3.4 Dielectric and piezoelectric properties of rhombohedral (011) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal [ $d_{32}$ mode]<sub>1</sub>

As well-known in the previous study results on PMN-PT piezoelectric single crystals,<sup>5-7,11</sup> piezoelectric charge constant ( $d_{32}$ ) and electromechanical coupling factor ( $k_{32}$ ) in the largest 31 mode were observed for a plate shape in  $d_{32}$  mode [length direction (100); width direction (011); thickness direction (011)] in the case of a rhombohedral piezoelectric single crystal. In the present study, (011) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal plates of  $5 \times 1.5 \times 0.5(t)$  mm size in  $d_{32}$  mode were also produced for measurement of dielectric and piezoelectric properties. According to Table 3 for the (011) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal, the electromechanical coupling factor ( $k_{32}$ ) was measured to be 0.77, piezoelectric charge constant ( $d_{32}$ ) about 630 [pC/N], piezoelectric voltage constant ( $g_{32}$ ) about 45 [ $\times 10^{-3}$  Vm/N], and elastic compliance ( $s_{22}^E$ ) about 48 [ $\times 10^{-12}$  m<sup>2</sup>/N]. Such high electromechanical coupling factor ( $k_{32}$ ) and piezoelectric voltage constant ( $d_{32}$ ) for a rhombohedral (011) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystal

**Table 3.** Dielectric and Piezoelectric Properties of Rhombohedral (011) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single Crystal Plates [5 × 1.5 × 0.5(t) mm<sup>3</sup>] at Room Temperature

k <sub>32</sub> Mode (LTF <sub>XY2</sub> )		[011] Ba(Ti <sub>0.92</sub> Zr <sub>0.08</sub> )O <sub>3</sub> Single Crystal Plates-Poled along the [011] axis					
		11	12	13	14	Average	STDEV.
Thickness	mm	0.50	0.50	0.50	0.50	0.50	0.00
Width	mm	1.50	1.50	1.50	1.50	1.5	0.00
Length	mm	5.00	5.00	5.00	5.00	5.0	0.00
Density	g/cm <sup>3</sup>	5.60	5.60	5.60	5.60	5.6	0.00
Capacitance	nF	0.211	0.209	0.208	0.212	0.210	0.002
tan d	/	0.008	0.007	0.009	0.008	0.008	0.000
f <sub>r</sub>	kHz	192.32	194.05	192.32	192.32	192.75	0.87
f <sub>a</sub>	kHz	265.52	265.52	267.91	267.91	266.71	1.38
Z <sub>r</sub>	kOhm	0.14	0.15	0.15	0.13	0.14	0.01
K <sub>3</sub> <sup>T</sup>	/	1,586	1,575	1,563	1,593	1,579	13
k <sub>32</sub>	/	0.772	0.764	0.780	0.780	0.77	0.01
d <sub>32</sub>	pC/N	636	621	637	644	634	9
g <sub>32</sub>	× 10 <sup>-3</sup> V m/N	45	45	46	46	45	1
s <sub>22</sub> <sup>E</sup>	× 10 <sup>-12</sup> m <sup>2</sup> /N	48.3	47.4	48.3	48.3	48.1	0.4
s <sub>22</sub> <sup>D</sup>	× 10 <sup>-12</sup> m <sup>2</sup> /N	19.5	19.7	18.9	18.9	19.3	0.4

showed higher values by more than twice compared with the values for general PZT polycrystalline ceramics. Consequently, the rhombohedral (011) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals showed the possibility for replacement of the linked piezoelectric PZT ceramics in diversified piezoelectric application areas using 31 or 32 mode.

#### 4. Conclusions

Rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals prepared by solid-state single crystal growth method showed excellent piezoelectric properties such as electromechanical coupling factor (k<sub>33</sub>) of higher than 0.85, piezoelectric charge constant (d<sub>33</sub>) of about 950 [pC/N], and piezoelectric voltage constant (g<sub>33</sub>) of about 41 [× 10<sup>-3</sup> Vm/N] in the case of 33 mode. And, the rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals in 32 [or 31] mode showed values such as electromechanical coupling factor (k<sub>32</sub>) of 0.77, piezoelectric charge constant (d<sub>32</sub>) of about 630 [pC/N], and piezoelectric voltage constant (g<sub>32</sub>) of about 45 [× 10<sup>-3</sup> Vm/N]. For poled (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals, phase transition temperature between rhombohedral phase and orthorhombic phase (T<sub>RO</sub>), that between orthorhombic phase and tetragonal phase (T<sub>OT</sub>) and that between tetragonal phase and cubic phase (T<sub>c</sub>) were observed to be 48, 71, and 109°C, respectively. The rhombohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals showed higher values for electromechanical coupling factors (k<sub>33</sub>, k<sub>32</sub>) and piezoelectric constants (d<sub>33</sub>, d<sub>32</sub>, g<sub>33</sub>, g<sub>32</sub>) than general PZT polycrystalline ceramics, although limitations in use range exist due to low phase transition temperatures, and hence are expected to be capable of replacing the linked piezoelectric PZT ceramics in diversified piezoelectric application areas. In particular, the rhom-

bohedral (001) Ba(Ti<sub>0.92</sub>Zr<sub>0.08</sub>)O<sub>3</sub> single crystals will allow application as an excellent lead-free piezoelectric material in the application areas where use of lead(Pb) harmful to human body and environments is difficult.

#### REFERENCES

1. B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics*; pp. 135~181, Academic Press, London and New York, 1997.
2. T. Takenaka, H. Nagata, and Y. Hiruma, "Current Development and Prospective of Lead-Free Piezoelectric Ceramics," *Jpn. J. Appl. Phys.*, **47** [5] 3787-801 (2008).
3. Y.-Q. Lu and Y.-X. Li, "A Review on Lead-Free Piezoelectric Ceramics Studies in China," *J. Adv. Dielectr.*, **1** [3] 269-88 (2011).
4. J.-F. Li, K. Wang, F.-Y. Zhu, L.-Q. Cheng, and F.-Z. Yao, "(K,Na)NbO<sub>3</sub>-Based Lead-Free Piezoceramics: Fundamental Aspects, Processing Technologies, and Remaining Challenges," *J. Am. Ceram. Soc.*, **96** [12] 3677-96 (2013).
5. S. Zhang and F. Li, "High Performance Ferroelectric Relaxor-PbTiO<sub>3</sub> Single Crystals: Status and Perspective," *J. Appl. Phys.*, **111** 031301-1-50 (2012).
6. S. Zhang, C. Randall, and T. R. Shrout, "Characterization of Perovskite Piezoelectric Single Crystals of 0.43BiScO<sub>3</sub>-0.57PbTiO<sub>3</sub> with High Curie Temperature," *J. Appl. Phys.*, **95** [8] 4291-95 (2004).
7. S. Zhang, S.-M. Lee, D.-H. Kim, H.-Y. Lee, and T. R. Shrout, "Elastic, Piezoelectric, and Dielectric Properties of 0.71Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.29PbTiO<sub>3</sub> Crystals Obtained by Solid-State Crystal Growth," *J. Am. Ceram. Soc.*, **91** [2] 683-86 (2008).
8. J. Li, Y. Li, Z. Zhou, R. Guo, and A. S. Bhalla, "Piezoelectric and Ferroelectric Properties of Lead-free Niobium-Rich Potassium Lithium Tantalate Niobate Single Crystals,"

- Mater. Res. Bull.*, **49** 206-9 (2014).
9. L. Zheng, X. Huo, R. Wang, J. Wang, W. Jiang, and W. Cao, “Large Size Lead-free (Na,K)(Nb,Ta)O<sub>3</sub> Piezoelectric Single Crystal: Growth and Full Tensor Properties,” *CrystEngComm*, **15** 7718-22 (2013).
  10. X. Huo, L. Zheng, S. Zhang, R. Zhang, G. Liu, R. Wang, B. Yang, W. Cao, and T. R. ShROUT, “Growth and Properties of Li, Ta Modified (K,Na)NbO<sub>3</sub> Lead-free Piezoelectric Single Crystals,” *Phys. Status Solidi Rapid Res. Lett.*, **10** 1-5 (2013).
  11. H.-Y. Lee, Development of High-Performance Piezoelectric Single Crystals by Using Solid-state Single Crystal Growth (SSCG) Method; pp. 158 in Handbook of Advanced Dielectric, Piezoelectric and Ferroelectric Materials, Edited by Z.-G. Ye (Ed.), CRC Press, New York, 2008.
  12. IEEE, ANSI/ IEEE Std. 176-1987: IEEE Standard on Piezoelectricity, The Institute of Electrical and Electronics Engineers, New York, 1988.