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Giant k_{31} Relaxor Single-Crystal Plate and Their Applications

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1. Introduction

Typical ferroelectric ceramics, lead zirconate titanate (PZT) ceramics are widely used for devices of electrical-mechanical energy conversion devices such as sensors and actuators, which correspond to the five senses and foot & hand of human being. Recently, these devices spread out in the computer controlled fields, for example, robotics and mechatronics. The research and development of ferroelectric ceramics, particularly PZT ceramics, have mainly focused on the material compositions to realize new electronic devices utilizing their piezoelectric properties. Many researchers in companies and institutes have carried out R & D on such chemical compositions since the discovery of piezoelectricity in PZT ceramics by Jaffe et al. in 1954. On the other hand, through the new research on DC poling field dependence of ferroelectric properties in PZT ceramics, the poling field has become an effective tool for evaluation and control of the domain structures, which fix the dielectric and ferroelectric properties of PZT ceramics. Therefore, PZT ceramics with different domain structures can be fabricated even though the ceramic compositions remain the same. These ceramics are called poling field domain controlled ceramic. It is thought that the domain controlled ceramics will lead to a breakthrough and the appearance of new ferroelectric properties. The study on the clarification of relationships between [compositions] vs [poling fields] vs [dielectric and piezoelectric properties] in hard and soft PZT ceramics was applied to other ferroelectric materials of lead titanate ceramics, lead-free ceramics such as barium titanate, alkali bismuth niobate, alkali bismuth titanate ceramics and relaxor single crystals of $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ (PZNT91/09) and $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.74}\text{Ti}_{0.26}]\text{O}_3$ (PMNT74/26) compositions.

This chapter describes how can be achieved the new ferroelectric properties such as giant transverse-mode electromechanical coupling factor of k_{31} over 80% and piezoelectric strain d_{31} constant of -2000 pC/N in PZNT91/09 and PMNT74/26 single crystals realized a mono-domain single crystal by accurately controlling the domain structures. In addition, high-efficiency piezoelectric unimorph and bimorph are also described as the devices using giant k_{31} single crystals.

2. Giant electromechanical coupling factor of k_{31} mode and piezoelectric d_{31} constant in $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ single-crystal plates

Ferroelectric single crystals made of compounds such as $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ (PZNT91/09) have been attracting considerable attention, because of the large longitudinal-

mode electromechanical coupling factor of k_{33} over 92%. Since high-quality and large crystals are necessary to develop devices such as transducers for medical use, we have undertaken and succeeded in the fabrication of PZNT91/09 single crystals with large dimensions. In addition, for further applications to sensors and actuators, a large k_{31} (d_{31}) mode as well as a large k_{33} (d_{33}) mode are needed.

2.1 Single-crystal sample preparation

The single crystals evaluated were grown by a solution Bridgman method with a Pt crucible supported at the bottom by a conical insulator stand. The crystals without Pt contamination from the crucible have the dimensions of 50 mm (2 inches) diameter, 35 mm height, and 325 g weight. The as-grown single crystals were cut along [100] of the original cubic direction confirmed by X-ray diffraction and from Laue photographs. The single-crystal samples with dimensions of $4.0^W(\text{width}) \times 13^L(\text{length}) \times 0.36^T(\text{thickness})$ mm for k_{31} , k_t and d_{31} and $4.2^W \times 4.2^L \times 12^T$ mm for k_{33} and d_{33} were prepared to evaluate the dielectric and piezoelectric properties. Gold electrodes for the following DC poling and electrical measurements were fabricated by conventional sputtering. Poling was conducted at 40 °C for 10 min by applying 1.0 kV/mm to obtain resonators with various vibration modes.

2.1.1 What is “giant k_{31} piezoelectricity”?

Figure 1 shows the frequency responses of the impedance in k_{33} and k_{31} modes in the cases of various coupling factors. It is easy to explain the wide frequency band, which corresponds to the difference between anti-resonant frequency (f_a) and resonant frequency (f_r), in higher coupling factors. An early work on a PZNT91/09 single crystal poled

Fig. 1. Frequency and phase responses of (a) k_{33} and (b) k_{31} fundamental modes in the cases of various coupling factors.

along [001] of the original cubic direction found that the values of k_{31} (d_{31}) and k_{33} (d_{33}) modes were 62% (-493 pC/N) and 92% (1570 pC/N), respectively. In a more recent work, the k_{31} (d_{31}) mode of 53% (-1100 pC/N) and the k_{33} (d_{33}) mode of 94% (2300 pC/N) were reported for $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}]\text{O}_3$ (PZNT92/08) single crystals poled along [001]. There are significant differences in the k_{31} and d_{31} modes between our result and the previous results, despite finding almost the same k_{33} (95%) and d_{33} (2500 pC/N).

A large difference between k_{31} =80.8% and $-d_{31}$ =1700 pC/N in this study and k_{31} =53-62% and $-d_{31}$ =493-1100 pC/N in the previous studies for the single crystals is considered to be due to the following. It is well known that dielectric and piezoelectric properties are strongly affected by the quality of the crystals. It was pointed out that a small portion of opaque parts in the crystal wafer significantly reduces the electromechanical coupling factor of the crystals. Since PZNT91/09 crystals evaluated in this study have very high transparency with a minimum defect level thus far reported, due to better control of the Bridgman crystal growth, the highest k_{31} and d_{31} can be obtained.

2.1.2 Where does “giant k_{31} piezoelectricity” come from?

Figures 2(a) and 2(b) show the temperature dependences of k_{31} , k_{33} and elastic compliance (s_{11}^E). Higher k_{31} and k_{33} were obtained in the rhombohedral phase below 80 °C. The values of s_{11}^E in the rhombohedral phase are larger than those in the tetragonal phase. Furthermore, the frequency constant ($fc=fr \times L$, where L is length), which corresponds to half the bulk wave velocity, of the k_{31} mode ($fc_{31}=522 \text{ Hz}\cdot\text{m}$) is relatively small in comparison with that of lead zirconate titanate (PZT) ceramics ($fc_{31}=1676 \text{ Hz}\cdot\text{m}$). We believe that the high piezoelectricity in the PZNT91/09 single crystal is due to the mechanical softness of the rhombohedral phase, not the existence of a MPB, for easy deformation by the poling field. This concept may be supported by the result that high k_{33} (>90%) independent of the rhombohedral composition, such as PZNT91/09, PZNT92/08 or $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}]\text{O}_3$ (PZNT95.5/4.5), was obtained.

Fig. 2. Temperature dependences of (a) electromechanical coupling factors (k_{31} and k_{33}) and (b) elastic compliance (s_{11}^E) in PZNT91/09 single crystal.

In conclusion of this part, frequency spectrum analysis of the responses to vibration modes was carried out in detail utilizing large PZNT91/09 single crystals of high quality. Giant k_{31} and d_{31} , as well as k_{33} and d_{33} , were obtained by efficient and uniform DC poling, it means a mono-domain structure in the single-crystal plate as described the next part. The crystals with these giant k_{31} and d_{31} will be applied for use in sensors and actuators with high performance.

2.2 Origin of giant piezoelectricity in PZNT91/09 single-crystal plates

In order to clarify the origin of giant piezoelectricity in PZNT91/09 single-crystal plates, the poling field dependence of dielectric and ferroelectric properties were investigated in single-crystal samples with demension of $4.0^W \times 13^L \times 0.36^T$ mm for k_{31} , k_t and d_{31} and $4.2^W \times 4.2^L \times 12^T$ mm for k_{33} and d_{33} . The poling field dependence was carried out as follows; the poling was conducted at 40 °C for 10 min while varying the poling field (E) from 0 to 2000 V/mm. After each poling, the dielectric and piezoelectric properties were measured at room temperature using an LCR meter, an impedance analyzer and a d_{33} meter. Moreover, the domain structures were observed under polarized light with crossed nicols by an optical microscope.

2.2.1 DC poling field dependence of dielectric constant, d_{33} constant, k_{31} , k_t , k_{33} and their frequency constants of fc_{31} and fc_t

Figure 3 shows the effect of DC poling field (E) on dielectric constant ($\epsilon_{33}^T/\epsilon_0$) and piezoelectric d_{31} and d_{33} constants. There were three stages in $\epsilon_{33}^T/\epsilon_0$ with increasing E . The first stage was $E < 400$ V/mm, the second stage was $400 \text{ V/mm} \leq E < 1000$ V/mm, and the third stage was $E \geq 1000$ V/mm. These stages in terms of dielectric constant mean that there are three thresholds of domain rotation and switching in the direction of the poling field. From our previous study, E of 300 V/mm in the first stage corresponds to the coercive field (E_c) and E of 180° domain clamping on PZNT91/09 single crystals. While d_{33} has approximately the same tendency as the dielectric constant for the poling field, d_{31} decreased abruptly over 1500 V/mm in the third stage. The giant $-d_{31}$ of nearly 1700 pC/N could be obtained at $1000 \text{ V/mm} \leq E < 1500 \text{ V/mm}$. On the other hand, the highest d_{33} of nearly 2500 pC/N could be obtained at $1000 \text{ V/mm} \leq E \leq 2000 \text{ V/mm}$. It was thought that the difference between d_{31} and d_{33} at $1500 \text{ V/mm} \leq E \leq 2000 \text{ V/mm}$ was due to the difference in the domain structure in the directions of the length and the thickness for the sample plate ($4.0^W \times 13^L \times 0.36^T$ mm).

Fig. 3. Poling field dependence of dielectric constant, and piezoelectric d_{31} and d_{33} constants (poling temperature: 40 °C, time: 10 min).

Figure 4 shows the effect of poling field (E) on the electromechanical coupling factors (k_{31} , k_{33}) and frequency constant (fc_{31}). The plots of the poling field vs k_{33} and k_{31} were almost the same as the plots of the poling field vs d_{33} and d_{31} shown in Fig. 3. While the giant k_{31} of over 80% was obtained at $1000 \text{ V/mm} \leq E < 1500 \text{ V/mm}$, the highest k_{33} of over 90% was obtained at $1000 \text{ V/mm} \leq E \leq 2000 \text{ V/mm}$. Furthermore, the frequency constant of the k_{31} mode (fc_{31}) showed the lowest value of nearly 500 Hz·m at $1000 \text{ V/mm} \leq E < 1500 \text{ V/mm}$. Therefore, it was found that the giant k_{31} (d_{31}) and the minimum fc_{31} appeared simultaneously at the specific poling fields of $1000 \text{ V/mm} \leq E < 1500 \text{ V/mm}$. With increasing E from 1500 V/mm to 2000 V/mm , k_{31} decreased and fc_{31} increased abruptly without any change in k_{33} . The behavior observed for the poling field vs k_{31} (d_{31}) and fc_{31} in the third region suggested that a mono-domain in the length direction (the direction perpendicular to the poling field) was achieved at $1000 \text{ V/mm} \leq E < 1500 \text{ V/mm}$, and further, the mono-domain changed into a number of domains (multi-domains in the plate) in the length direction at $1500 \text{ V/mm} \leq E \leq 2000 \text{ V/mm}$.

Fig. 4. Poling field dependence of k_{31} and k_{33} , and frequency constant fc_{31} (poling temperature: 40°C, time: 10 min).

Figure 5 shows the effect of poling field (E) on electromechanical coupling factor (k_t) and frequency constant (fc_t). The k_t mode and fc_t correspond to the thickness vibration for the sample plate ($4.0^W \times 13^L \times 0.36^T$ mm). While k_{33} increased from 80% to 95% with increasing E from 400 V/mm to 2000 V/mm in Fig. 4, k_t and fc_t were independent of the poling field in the same range of E . We believe the difference in the poling field dependence between k_{33} and k_t is due to the effect of the domain structure on the vibrations of k_{33} and k_t modes in the thickness direction for the sample plate.

Fig. 5. Poling field dependence of k_t and frequency constant fc_t (poling temperature: 40 °C, time: 10 min).

2.2.2 Domain structures of single-crystal plates at various poling fields

After each poling at E , both the surfaces of the sample plate ($4.0^W \times 13^L \times 0.36^T$ mm) were polished and the domain structure in the plate area ($4.0^W \times 13^L$ mm) was observed under polarized transmission light with crossed nicols. The frequency responses of the impedance in k_{31} mode were also measured at every poling field. Figures 6(a)~6(d) show the domain structures and the frequency responses in k_{31} mode. The as-grown crystal mainly had black and brown stripes as shown in Fig. 6(a). We believe that the stripes consist of 180° domains alongside their domain walls. By applying E of 350 V/mm for 10 min at 40°C , the brown area increased, the boundaries between black and brown stripes became unclear and the single response of the k_{31} (47%) mode was obtained [Fig. 6(b)]. A mono-domain crystal without domain walls was confirmed to exist at $E=1000$ V/mm. In addition, the giant k_{31} of nearly 80% appeared in the mono-domain crystal with the single response and with the minimum frequency constant of fc_{31} mode [Fig. 6(c)]. The

Fig. 6. Poling field dependence of domain structures in sample plate area ($4.0^W \times 13^L$ mm) and frequency responses of impedance and phase on k_{31} mode; (a) as-grown (before poling), (b) $E=350$ V/mm, (c) $E=1000$ V/mm and (d) $E=2000$ V/mm; the thickness of the plate is 0.36 mm and the broken line in Fig. 6(d) indicates a domain boundary.

frequency constant (fc_{31}) corresponds to half the bulk wave velocity (v_{31}), and further, there is a relationship between the Young’s modulus (Y) of the crystal and fc_{31} as follows:

$$v_{31} = 2 \times fc_{31} = 2 \times fr \times L = Y^{1/2} \cdot \rho^{-1/2},$$

where fr and ρ are the resonant frequency of k_{31} mode and the bulk density of the crystal, respectively. Therefore, it is said that the most softened (i.e., with the lowest v_{31} or fc_{31}) PZN91/PT09 crystals poled by the specific poling conditions ($1000 \text{ V/mm} \leq E < 1500 \text{ V/mm}$ at 40°C for 10 min) are essential to achieve the giant k_{31} and d_{31} . With E greater than 1500 V/mm , since the mono-domain changed into the muluti-domains, the single response of the k_{31} mode was divided into two responses and the value of fr or fc_{31} increased. As a consequence, k_{31} was reduced to 63% [Fig. 6(d)]. It was thought that the reason only a few domains were formed was the generation of strain in the direction perpendicular to the poling field - namely, not in the sample thickness of 0.36^T mm but in the sample plate area of $4.0^W \times 13^L \text{ mm}$, in the crystal poled by the higher poling field. This is summarized schematically in Fig. 7 for the relationships among the poling fields and the domain structures. In addition, Table 1 shows the relationships among the Young’s modulus (Y), k_{33} and k_{31} for various materials. It is found that the Y ($0.89 \times 10^{10} \text{ N/m}^2$) in rhombohedral PZNT91/09 with giant k_{31} is one order of magnitude smaller than the Y ($6 \sim 9 \times 10^{10} \text{ N/m}^2$) of PZT ceramics and, roughly speaking, one order of magnitude larger than the Y ($0.05 \times 10^{10} \text{ N/m}^2$) of rubber. Therefore, we believe that the giant k_{31} of over 80% arises from the remarkable softness of the domain controlled single crystal due to the poling field.

Fig. 7. Schematics of domain structures (↘↘↘) in PZNT91/09 single crystal under various poling fields; the arrow of E shows the direction of the poling field.

Material	$Y (\times 10^{10} \text{ N/m}^2)$	$k_{33} (\%)$	$k_{31} (\%)$
PZNT 91/09	0.89* (2.58)**	95	80
Soft PZT ceramics	6	70	40
Hard PZT ceramics	9	60	30
PbTiO ₃ ceramics	13	50	6
BaTiO ₃ ceramics	11	45	15
Steel	20	—	—
Rubber	0.05	—	—

*Rhombohedral phase, **Tetragonal phase.

Table 1. Relationships among Young’s modulus (Y), k_{33} and k_{31} in various materials.

In conclusion of this part, the origin of PZNT91/09 single crystals with giant k_{31} of over 80% and $-d_{31}$ constant nearly 1700 pC/N were due to a mono-domain structure in the crystal plates. Controlling the poling conditions, the crystal plate with multi-domains changed into one having the mono-domain in the direction perpendicular to the poling field as well as in the direction parallel to the poling field. Futhermore, this ferroelectric domain controlled single crystal by a poling field possessed the lowest frequency constant of fc_{31} .

3. Giant k_{31} in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ single-crystal plates

Another relaxor single crystal of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMNT) is investigated in detail regarding the k_{31} mode and the conditions for obtaining giant k_{31} and d_{31} constant are clarified.

3.1 Crystal plane dependence of giant k_{31} in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ single-crystal plates

Recently, a giant k_{31} over 86% and a piezoelectric d_{31} constant of nearly -2100 pC/N were found for a (100) $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ (PZNT91/09) single crystal poled in the [001] direction. In order to realize giant k_{31} , it was the significant relationship between the crystal plane and the poling direction. Moreover, it was clarified that the giant k_{31} and d_{31} constant could be obtained with a poling temperature of 40 °C in the rhombohedral phase and with sufficient poling fields of 1000~1500 V/mm. The origin of the giant k_{31} and d_{31} constant was found to be due to the mono-domain structure in the direction perpendicular to the poling field as well as in the direction parallel to the poling field. In this part, we investigate the relationships between the crystal planes and the poling direction in $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$ [PMNT(1-x)/x] single-crystal plates to obtain giant k_{31} .

3.1.1 Realization of giant k_{31} in PMNT plates

Figure 8 shows the DC poling field (E) dependence of relative dielectric constant (ϵ_r) and k_{31} in (100) PMNT68/32 and (110) PMNT74/26 single-crystal plates. The ϵ_r (■) in (100) PMNT has a peak at E=300 V/mm and decreases with increasing E. There is aging in ϵ_r (■) and k_{31} (□) for (100) PMNT, after 16 and 64 h at room temperature. The same phenomena were observed in (110) PZNT91/09 single-crystal plates poled in the [110] direction. On the other hand, the ϵ_r (●) and k_{31} (○) in (110) PMNT increased abruptly at E=200 V/mm and reached constant values without aging. It was found that a giant k_{31} of over 86% was obtained at $E \geq 200$ V/mm in (110) PMNT single-crystal plates at the poling temperature of 40 °C.

Fig. 8. DC poling field dependence of ϵ_r and k_{31} in (100) and (110) PMNT single-crystal plates.

The effects of poling temperature on k_{31} , d_{31} constant and the frequency constant (half of the bulk wave velocity) of the k_{31} mode (fc_{31}) in (110) PMNT74/26 single-crystal plates are shown in Fig. 9. The temperatures of 40 °C (○), 100 °C (□) and 120 °C (△) correspond to the pseudo-cubic phase, the phase boundary between pseudo-cubic and tetragonal phases, and the tetragonal phase, respectively (Fig. 10). It is confirmed that giant k_{31} and d_{31} constant were obtained to polarize (110) PMNT plates in pseudo-cubic phase (the poling temperature of 40 °C), while applying $E \geq 200$ V/mm. In addition, the giant k_{31} and d_{31} constant were accompanied by the lowest fc_{31} , nearly 700 Hz·m. These results were the same as those of (100) PZNT91/09 single-crystal plates with giant k_{31} .

Fig. 9. DC poling field dependence of k_{31} , d_{31} and fc_{31} in (110) PMNT74/26 single-crystal plates at poling temperatures of 40 °C (○), 100 °C (□) and 120 °C (△).

Fig. 10. Phase diagram of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ single crystals grown by a solution Bridgman method.

3.1.2 Impedance response analysis of giant k_{31}

Figures 11(a), (b) and Figs. 12 (a), (b) show the frequency responses of impedance on the fundamental k_{31} modes and up to 500 kHz in the cases of (100) and (110) PMNT single-crystal plates poled at 40 °C, $E=1000\text{ V/mm}$ and 10 min. The values of k_{31} in (100) and (110) PMNT single-crystal plates were 42.6% and 84.6% (giant k_{31}), respectively. The k_{31} fundamental and its overtones were observed to have complicated spurious responses in (100) PMNT in Fig. 12(a). However, the k_{31} fundamental and its 3rd, 5th, 7th and 9th overtones were confirmed not to have spurious responses in (110) PMNT with giant k_{31} in Fig. 12(b), and were also confirmed the frequency responses of impedance in (100) PZNT91/09 single-crystal plates with giant k_{31} . Therefore, it is found that a single vibration was generated in the direction of the length (L). In order to clarify the resonance response near 300 kHz [inside the ellipse in Fig. 12(b)], the original single-crystal plate ($13^L\times4.0^W\times0.47^T\text{ mm}$) was cut to the small plate dimensions ($0.97^L\times4.0^W\times0.47^T\text{ mm}$). The k_{32} in

Fig. 11. Impedance and phase responses of the fundamental k_{31} mode in (a) (100) and (b) (110) PMNT single-crystal plates.

Fig. 12. Frequency responses of impedance in fully poled (a) (100) and (b) (110) PMNT single-crystal plates (DC poling conditions: 40 °C, 1000 V/mm, 10 min).

the width (W) direction was 69%, which was calculated from the resonance response of the small plate. Furthermore, the frequency constants on the k_{31} (length direction) and k_{32} (width direction) modes became 680 Hz·m and 1425 Hz·m, respectively. Consequently, it was found that the (110) PMNT single-crystal plate with giant k_{31} possessed an anisotropy in the frequency constant on the 13·x4.0^W mm plate and consisted of a mono-domain as in the case of the (100) PZNT91/09 single-crystal plate with giant k_{31} .

3.1.3 Relationship between crystal plane and poling direction

The mechanism for realizing giant k_{31} can be explained by using the crystal plane and poling direction. Figure 13 shows the relationship between the crystal plane, which determines the direction of the spontaneous polarization, and the poling direction in (100) and (110) PMNT single-crystal plates. While applying the poling field to the (100) PMNT single-crystal plate at a poling temperature of 40 °C (pseudo-cubic phase), the poling field only acts to expand the x-axis in the direction of the poling field. In the (110) PMNT plate, the poling field acts to generate strain via the expansion of the x and y-axes (Fig. 13), which moves the ferroelectric domains on the (110) plane. While the domain structure on the (110) plane became singular due to the generated strain, it is thought that the anisotropy of the frequency constants on the k_{31} and k_{32} modes appeared and the giant value of the k_{31} mode in (110) PMNT was achieved through the poling process.

Fig. 13. Relationship between crystal plane, direction of the spontaneous polarization and poling direction in (100) and (110) PMNT single-crystal plates at 40 °C (pseudo-cubic phase).

Table 2 shows the values of k_{31} , k_{32} , d_{31} and d_{33} constants in PMNT and PZNT single-crystal plates with various crystal planes. Although giant k_{31} and d_{31} constant were obtained in the (110) PMNT plate, a large d_{33} constant (2420 pC/N) was realized in the (100) PMNT plate. On the other hand, giant k_{31} , d_{31} constant, and large d_{33} constant (2400 pC/N) were obtained simultaneously in the (100) PZNT91/09 plate. Therefore, it was clarified that giant k_{31} , d_{31} and d_{33} constants appeared in the peculiar combination of the crystal plane and poling direction in the relaxor single crystals. Moreover, there was anisotropy on the k_{31} (length direction) and k_{32} (width direction) modes in (110) PMNT with giant k_{31} as well as in (100) PZNT with giant k_{31} .

Crystal plane	Single crystal	k_{31} (%)	$-d_{31}$ (pC/N)	k_t (%)	d_{33} (pC/N)	k_{32} (%)	Pr ($\mu\text{C}/\text{cm}^2$)	Ec (V/mm)	Aging
(100)	PZNT	86	2100	55	2400	42	35	600	Good
(100)	PMNT	65	1030	60	2420		22	300	NG
(110)	PZNT	30~60	300~720	40	530~1030				NG
(110)	PMNT	87	1320	48	970	69	30	200	Good
(111)	PZNT	20	~170	50	190~560				Good

Table 2. Giant k_{31} and d_{31} constant in PMNT and PZNT single-crystal plates with various crystal planes. k_t is the coupling factor of thickness vibration in a plate, and piezoelectric d_{33} constant was measured with a d_{33} meter.

In conclusion of this part, giant k_{31} over 86% in (110) PMNT single-crystal plates was realized in order to control the relationship between the crystal plane, which determines the direction of the spontaneous polarization, and the poling direction. The plate with giant k_{31} shows the impedance responses with a single vibration generated in the length direction. It is thought that the origin of giant k_{31} is the mono-domain structure in the plate.

3.2 Chemical composition dependence of ginat k_{31} in PMNT single-crystal plates
A giant electromechanical coupling factor of k_{31} mode of more than 86% was found for (100) $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ (PZNT91/09) single-crystal plates ($13^{\text{L}}\times 4.0^{\text{W}}\times 0.36^{\text{T}}$ mm) and (110) $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.74}\text{Ti}_{0.26}]\text{O}_3$ (PMNT74/26) single-crystal plates ($13^{\text{L}}\times 4.0^{\text{W}}\times 0.47^{\text{T}}$ mm) poled in the [001] and [110] directions, respectively. In this part, the chemical composition dependence of k_{31} mode in PMNT single-crystal plates with (110) plane is investigated in detail and furthermore, the relationships between the crystal phase after poling and giant k_{31} are clarified.

3.2.1 Ti composition dependence of ginat k_{31}
The (110) $\text{PMNT}(1-x)/x$ ($x=0.251\sim 0.301$) single-crystal plates in this study have pseudo-cubic phase before poling below 100 °C ($x=0.25$) and 90 °C ($x=0.30$). Figure 14 shows the relationships between relative dielectric constant (ϵ_r) before and after poling [Fig. 14(a)], k_{31} and the frequency constant (half the bulk wave velocity) of k_{31} mode (fc_{31}) [Fig. 14(b)], and the electromechanical coupling factor of the thickness vibration mode of the plate (k_t) and frequency constant of k_t mode (fc_t) [Fig. 14(c)] versus Ti composition (x) in (110) $\text{PMNT}(1-x)/x$ single-crystal plates. Although ϵ_r (○) in (110) PMNT is almost constant and abruptly increases for $x>0.293$ before poling, ϵ_r (●) after poling is divided into four groups 1~4: group 1 ($x=0.251\sim 0.255$), group 2 ($x=0.269\sim 0.279$), group 3 ($x=0.291\sim 0.293$) and group 4

($x=0.296\sim0.301$) in Fig. 14(a). Since the groups of ϵ_r correspond to the groups of the domain structure, it was thought that the PMNT single-crystal plates processed different domain structures in each group after DC poling. On the other hand, k_{31} increases with an increase in x and reaches a maximum of 92% at $x=0.291$. After that, k_{31} suddenly decreases with x as shown in Fig. 14(b). The fc_{31} also has four groups and shows an opposite tendency compared with k_{31} vs x . This means that higher k_{31} is obtained for lower fc_{31} , because the decrease in the number of domain boundaries through the improvement of the poling process in the single-crystal plates leads to a decrease in stiffness. Since k_t and fc_t are independent of x in Fig. 14(c), the domain structures are almost the same in the thickness direction of the plates. Therefore, the chemical composition dependence of ϵ_r after poling, k_{31} and fc_{31} appears to be dependent on the domain structure in the plate ($13^L\times4.0^W$ mm).

Fig. 14. Ti composition dependence of (a) ϵ_r before and after poling, (b) k_{31} , fc_{31} and (c) k_t , fc_t in PMNT(1-x)/x single-crystal plates.

3.2.2 Impedance response analysis of giant k_{31}

Figure 15 shows the frequency responses of impedance to 500 kHz in the cases of groups 1~4 in Fig. 14. The k_{31} fundamental and their odd-number overtones of 3rd, 5th, 7th and 9th with the k_{32} fundamental vibration (width direction) were confirmed without spurious responses in groups 1~3 in (110) PMNT with giant k_{31} , as well as the frequency response of impedance in the (100) PZNT91/09 single-crystal plate with giant k_{31} . However, the k_{31} fundamental and their overtones were observed with complicated spurious responses in group 4 in the (110) PMNT with $k_{31}=60\%$. Therefore, it was found that a single vibration is generated in the direction of the length (L) in the (110) PMNT with giant k_{31} , similar to the case of the (100) PZNT91/09 single-crystal plate with giant k_{31} .

Fig. 15. Frequency responses of impedance in fully poled (110) PMNT(1-x)/x single-crystal in cases of (a) group 1, (b) group 2, (c) group 3 and (d) group 4 (●1: k_{31} fundamental vibration, ●3-9: k_{31} odd-number overtones, ○1: k_{32} fundamental vibration; DC poling conditions: 40°C, 1000 V/mm, 10 min).

3.2.3 Crystal phase to realize giant k_{31}

A mechanism to realize giant k_{31} can be explained by the crystal plane, which strongly affects the direction of the spontaneous polarization and poling direction. Giant k_{31} in relaxor single-crystal plates can be achieved when the poling field generates sufficient strain to move the ferroelectric domains in the plates ($13^L \times 4.0^W$ mm), not merely to expand the spontaneous polarization axes in the direction of the poling field. We will

discuss in detail the relationships between crystal planes, spontaneous polarization axes and poling direction in (110) PMNT single-crystal plates (groups 1~4) in comparison with the cases of (100) and (110) PZNT91/09 single-crystal plates (see Fig. 27 in the paragraph 4.2.3). Furthermore, it will be clarified that the crystal phases after poling can be estimated by the value of k_{31} and the combination between the directions of the spontaneous polarization axes and the poling field, which generates the strain sufficient to move the domains in the plates.

In conclusion of this part, giant k_{31} of more than 80% in (110) PMNT single-crystal plates was clarified to possess Ti composition dependence. The frequency response of impedance in (110) PMNT single-crystal plates with giant k_{31} was composed of a single vibration in the length direction. In addition, the domain movement to realize giant k_{31} in the crystal plate was due to the combination between the direction of the spontaneous polarization and the poling direction.

4. Other characteristics investigation

The giant k_{31} and d_{31} constant in the PZNT91/09 and PMNT(1-x)/x single-crystal plates were due to the generation of a single vibration in the length direction. However, there is as yet no evidence of the close relationship between the mono-domain plate with a giant k_{31} , which means a single vibration body, and the single vibration in the plates measured from the impedance response.

Furthermore, the P-E hysteresis loops and the relationship to electric field (E) vs strain measurement were investigated from the viewpoints of giant k_{31} .

4.1 Frequency response analysis by finite element method in relaxor single-crystal plates with giant k_{31}

In this part, the frequency response analysis of impedance on the giant k_{31} mode is evaluated by a finite element method (FEM) in order to characterize the mono-domain plates. Since the number of ferroelectric domains in the plates corresponds to the number of piezoelectric vibration bodies, the frequency response analysis by FEM was applied to the evaluation of their domain structures. Moreover, the domain behavior of the PZNT91/09 single-crystal plates is also investigated by FEM, particularly focusing on the 3rd overtone of the k_{31} fundamental vibration.

4.1.1 FEM application

Resonators composed of relaxor single-crystal plates, the dimensions of which are $13^L \times 4.0^W \times 0.36^T$ mm, with a giant k_{31} in PZNT91/09 with the (100) plane and PMNT74/26 with the (110) plane were analyzed using a commercial analysis program (ANSYS) by FEM. For the FEM simulation, an electric field of 1.0 V/mm to simulate the impedance responses was added in the thickness direction of the plate resonators because the actual voltage to be measured was 0.5 V by the impedance analyzer. The material constants obtained from the measured and reference data on the relaxor single crystals were used to calculate the impedance responses. The numbers of the elements and nodes for FEM were 800 pieces and 4271 points, respectively. Piezoelectric equations were applied to the orthorhombic phase. Furthermore, Poisson ratio in the length direction (k_{31} mode) and width direction (k_{32} mode)

was measured from the impedance responses by single-crystal plate resonators with different dimensions. In order to evaluate domain structures in the single-crystal plates, the relationships between the number of domains in the PZNT91/09 single-crystal plates and the 3rd overtone splitting of the k_{31} fundamental vibration were also investigated by FEM simulation.

Table 3 shows the coupling factors of k_{31} , k_{32} and their frequency constants ($f_r \times L$ or W , where f_r is the resonant frequency) of fc_{31} , fc_{32} in the relaxor single-crystal plates with a giant k_{31} of more than 80%. The values of σ_W^E/σ_L^E in Table 3 were calculated from the elastic compliance of s_{11}^E and s_{22}^E because $\sigma_L^E=-(s_{12}^E/s_{11}^E)$ and $\sigma_W^E=-(s_{12}^E/s_{22}^E)$, where σ_L^E and σ_W^E are the Poisson ratios in the directions of length (13 mm) and width (4 mm), respectively. In the simulation, σ_W^E/σ_L^E was used to evaluate the crystal anisotropy of the relaxor single crystals, because of the difficulty in measuring the values of s_{12} in the single crystals. It was confirmed that there are large crystal anisotropies of s_{11}^E and s_{22}^E between the L and W directions and large differences in σ_W^E/σ_L^E of 3.4 (PZNT91/09) and 4.5 (PMNT74/26), respectively.

single crystal	k_{31} (%)	k_{32} (%)	fc_{31} (Hz·m)	fc_{32} (Hz·m)	s_{11}^E (10^{-12} m ² /N)	s_{22}^E (10^{-12} m ² /N)	σ_W^E/σ_L^E
PZNT91/09	86	42	520	830	110	32	3.4
PMNT74/26	87	69	683	1425	67	15	4.5

Table 3. Material constants of relaxor single-crystal plates with giant k_{31} .

Although the values of k_t (coupling factor of plate thickness vibration) and fc_t (frequency constant of the k_t mode) of the PZNT91/09 and PMNT74/26 single-crystal plates with a giant k_{31} were 57, 49% and 2087, 2588 Hz·m, respectively, it was thought the crystal structure of the plate resonators after DC poling becomes a field-induced phase such as the orthorhombic phase, because of the anisotropy of the bulk wave velocities (twofold the frequency constant) in the length ($L=13$ mm), width ($W=4.0$ mm) and thickness ($T=0.36$ mm) directions. Furthermore, a giant k_{31} could be obtained only in the orthorhombic phase after DC poling from the relationships between the directions of the spontaneous polarization and DC poling field to move domains in the plate ($13^L \times 4.0^W$ mm).

4.1.2 Simulation of k_{31} and k_{32} modes by FEM

The change in the values of σ_W^E and σ_L^E affected the frequency response of impedance on k_{31} fundamental vibration, the overtones, and k_{32} fundamental vibration in the frequency range of 0~500 kHz. The simulated response at $\sigma_W^E/\sigma_L^E=3.2$ ($\sigma_L^E=0.089$, $\sigma_W^E=0.29$) and $s_{12}^E=-10$ (10^{-12} m²/N) was well fitted to the measured responses, as shown by the arrows in Fig. 16, in the case of the PZNT91/09 single-crystal plate. The simulated data at $\sigma_W^E/\sigma_L^E=4.9$ ($\sigma_L^E=0.041$, $\sigma_W^E=0.20$) and $s_{12}^E=-3$ (10^{-12} m²/N) in the PMNT74/26 single-crystal plates also showed the same result (Fig. 17). In the calculations, the values of s_{12}^E were chosen to fit the simulated responses to the measured responses. Moreover, the Poisson ratio affected the value of k_{31} as well as the frequency response of impedance.

Fig. 16. Frequency responses of impedance on k_{31} and k_{32} modes in PZNT91/09 single-crystal plates; (a) measured and (b) simulated data.

Fig. 17. Frequency responses of impedance on k_{31} and k_{32} modes in PMNT74/26 single-crystal plates; (a) measured and (b) simulated data.

4.1.3 Simulation of k_t mode by FEM

The impedance responses up to 30 MHz in Fig. 18 were calculated in the PZNT91/09 single-crystal plates at $\sigma_W^E/\sigma_L^E=3.2$, $\sigma_L^E=0.045\text{-}0.13$, and $\sigma_W^E=0.15\text{-}0.41$. The k_t fundamental vibration and the 3rd and 5th overtones of the k_t fundamental vibration were observed between $\sigma_L^E=0.063\text{-}0.11$ and $\sigma_W^E=0.20\text{-}0.35$. In particular, sharp responses of the k_t fundamental vibration and the 3rd overtone were obtained between $\sigma_L^E=0.080\text{-}0.098$ and $\sigma_W^E=0.26\text{-}0.32$. The simulated coupling factor of $k_t=64\%$ was higher than that of $k_t=57\%$ calculated from the measured response. It was clarified that the large difference in $\sigma_W^E/\sigma_L^E=3.2$ and the suitable values of the elastic compliance, particularly $-s_{12}^E=9\text{-}11$ (10^{-12} m²/N), were key factors for the appearance of the k_t fundamental vibration and overtones.

The simulated response of the PMNT74/26 single-crystal plates is shown in Fig. 19 at $\sigma_W^E/\sigma_L^E=4.9$ ($\sigma_L^E=0.041$, $\sigma_W^E=0.20$) and $s_{12}^E=-3$ (10^{-12} m²/N). The fundamental k_t mode ($k_t=65\%$) and the 3rd overtone were observed independent of $-s_{12}^E$ values between 1~7 (10^{-12} m²/N). In the calculations, the values of $-s_{12}^E$ were chosen at a Poisson ratio (σ_W^E) within 0~0.5.

Fig. 18. Frequency responses of impedance on k_t mode in PZNT91/09 single-crystal plates; calculation for (a) $\sigma_W^E/\sigma_L^E=3.2$ ($\sigma_L^E=0.13$, $\sigma_W^E=0.41$)/ $s_{12}^E=-14$ (10^{-12} m²/N) and (b) $\sigma_W^E/\sigma_L^E=3.2$ ($\sigma_L^E=0.089$, $\sigma_W^E=0.29$)/ $s_{12}^E=-10$ (10^{-12} m²/N).

Fig. 19. Frequency responses of impedance on k_t mode in PMNT74/26 single-crystal plates; calculation for $\sigma_W^E/\sigma_L^E=4.9$ ($\sigma_L^E=0.041$, $\sigma_W^E=0.20$) and $s_{12}^E=-3$ (10^{-12} m²/N).

Figure 20 shows the impedance and phase responses of k_t fundamental vibration in the PZNT91/09 single-crystal plates. The impedance response consisted of four peaks split into ①-④ in the cases of the simulated and the measured responses. Herein, the PZNT91/09 plate resonator with a giant k_{31} of 84% was prepared under the poling conditions of a DC poling field (E) of 1200 V/mm. Although the simulation for the splitting was calculated from the values of $\sigma_W^E/\sigma_L^E=3.2$ ($\sigma_L^E=0.089$, $\sigma_W^E=0.29$) and $s_{12}^E=-10$ (10^{-12} m²/N), the splitting of the four peaks occurred in the case of a giant k_{31} in the PZNT91/09 single-crystal plates. Therefore, it was confirmed that the simulation data were exactly fitted to the measured data in both the

cases of the generation of the k_t mode and the impedance and phase responses of the k_t fundamental vibration. The impedance and phase responses of the k_t fundamental vibration of PMNT74/26 single-crystal plates are shown in Fig. 21 [$\sigma_W^E/\sigma_L^E=4.9$ ($\sigma_L^E=0.041$, $\sigma_W^E=0.20$) and $s_{12}^E=-3$ (10^{-12} m²/N)] in comparison with the measured responses. The simulated impedance and phase responses were well fitted to the measured responses.

Fig. 20. Frequency responses of impedance and phase on k_t fundamental vibration in PZNT91/09 single-crystal plates; (a) measured and (b) simulated data.

Fig. 21. Frequency responses of impedance and phase on k_t fundamental vibration in PMNT74/26 single-crystal plates; (a) measured and (b) simulated data.

4.1.4 Domain behavior evaluation by FEM

The 3rd overtone in the k_{31} mode was calculated to synthesize one-third of the simulated responses each in the cases of (i) $\sigma_W^E/\sigma_L^E=2.5$ ($\sigma_L^E=0.13$, $\sigma_W^E=0.32$), (ii) $\sigma_W^E/\sigma_L^E=2.4$ ($\sigma_L^E=0.13$, $\sigma_W^E=0.31$), and (iii) $\sigma_W^E/\sigma_L^E=1.8$ ($\sigma_L^E=0.17$, $\sigma_W^E=0.31$). The simulated 3rd overtone response consisted of three peaks splitting in PZNT91/09 [shown in the circle of Fig. 22(a)]. On the other hand, the plate resonator DC poled at $E=400$ V/mm, the poling field of which is just below that required to obtain a giant k_{31} , also possesses the 3rd overtone with three peaks splitting [shown in the circle of Fig. 22(b)]. Therefore, it was thought that the PZNT91/09 single-crystal plate was composed of three vibration bodies, namely, three large domains with σ_W^E/σ_L^E values of 2.5, 2.4, and 1.8. Since the splitting of the three peaks of the 3rd overtone response formed one peak at $E=1200$ V/mm obtaining a giant k_{31} of 84.4% (shown in the circle of Fig. 22(c)), it was proved that a mono-domain plate with a giant k_{31} was achieved. From our study, it was confirmed that frequency response analysis of impedance is an effective tool for the evaluation of domain structures in single-crystal plates.

Fig. 22. Frequency responses of impedance on 3rd overtone on k_{31} mode in PZNT91/09 single-crystal plates; (a) simulated data, (b) measured data of plate resonator DC poled at $E=400$ V/mm, and (c) measured data of plate resonator DC poled at $E=1200$ V/mm.

4.1.5 Origin of giant k_{31} from viewpoints of material constants

The most significant factors for realizing giant piezoelectricity in the k_{31} mode in the relaxor single-crystal plates were thought as follows: Firstly, large s_{11}^E values of 110 (10^{-12} m²/N) in the PZNT91/09 single-crystal plates and 67 (10^{-12} m²/N) in the PMNT74/26 single-crystal plates in the direction of length were required (Table 3). These s_{11}^E values are relatively

larger than that of 11-17 ($10^{-12} \text{ m}^2/\text{N}$) in PZT ceramics. This means that the single-crystal plates with a giant k_{31} of more than 80% became markedly soft and showed a low Poisson ratio, particularly $\sigma_L^E < 0.1$ after DC poling. Secondly, a large anisotropy of bulk wave velocity (twofold the frequency constant) accompanied by a large $\sigma_W^E/\sigma_L^E = 3.2\text{-}3.4$ in PZNT91/09 single-crystal plates and a large $\sigma_W^E/\sigma_L^E = 4.5\text{-}4.9$ in PMNT74/26 single-crystal plates was essential. Therefore, it was thought that the physical meaning of the above-mentioned large s_{11}^E , low σ_L^E , and large σ_W^E/σ_L^E originated from a field-induced phase such as the orthorhombic phase by DC poling because the combination of the directions of spontaneous polarization and poling field in the orthorhombic phase could only move domains in the plates.

In conclusion of this part, impedance response analysis by FEM was performed using the k_{31} , k_{32} , and k_t modes in relaxor single-crystal plates with a giant k_{31} . It was found that a large anisotropy on the k_{31} and k_{32} modes was generated in the plate resonators with a giant k_{31} . As the Poisson ratios of the length and width directions in the plates were changed, the simulation results were well fitted to the measured impedance responses. These results could be explained by the material constants in a field-induced phase induced by the DC poling field. Furthermore, the domain behavior in the single-crystal plates was evaluated from the synthesized impedance response of three vibration bodies, i.e., three domains with different Poisson ratios.

4.2 Giant k_{31} and d_{31} in relaxor single-crystal plates evaluated using P-E hysteresis loops and strain

The longitudinal-mode electromechanical coupling factor k_{33} of over 90% was easy to obtain because the vibration direction of the k_{33} mode is the same as that of the poling field. However, the relationship between the giant k_{31} and k_{33} modes is not clarified. In this part, we could explain the relationship using P-E hysteresis loops and electric field (E) vs strain measurement from the viewpoint of giant k_{31} .

4.2.1 P-E hysteresis loops

Figure 23 shows the electric field (E) dependence of P-E hysteresis loops in (100) PZNT91/09 single-crystal plate measured at 40°C by a high voltage test system. While a symmetrical P-E loop was observed at $E = 1000 \text{ V/mm}$, a triple loop was generated as $E \geq 1500 \text{ V/mm}$ in the case of the crystal plate with giant k_{31} .

Fig. 23. P-E hysteresis loops in PZNT91/09 single-crystal plates (a) before ($E = 1000 \text{ V/mm}$) and (b) after ($E = 1500 \text{ V/mm}$) the appearance of giant k_{31} over 80%.

Therefore, it was considered that the E of 1500 V/mm is a coercive field to obtain giant k_{31} . In addition, the triple loops were realized at 20-60 °C, in the rhombohedral phase of PZNT91/09.

Figure 24 shows the Ti composition (x) dependence of k_{31} [Fig. 24(a)] and P-E loops [Fig. 24(b)] in PMNT(1-x)/x single-crystal plate measured at 40 °C (pseudo-cubic phase) under E =1500 V/mm. Although a symmetrical P-E hysteresis loop was obtained at x = 0.296-0.301 in the plate with k_{31} =60%, triple loops were observed at x=0.273-0.293, and asymmetrical loops were observed at x=0.251-0.262 in the plates with giant k_{31} (>80%). The E=800 V/mm to generate the triple and asymmetrical loops corresponds to a coercive field to realize giant k_{31} .

Fig. 24. Ti composition (x) vs (a) k_{31} and (b) P-E hysteresis loops in PMNT(1-x)/x single-crystal plates; x=0.251 (asymmetrical part near dotted lines), x=0.273/ 0.293 (triple loop at high E), and x=0.296 (symmetrical loop).

4.2.2 Shrinkage strain characteristics

Figure 25 shows the dependence of the shrinkage strain measured at room temperature (rhombohedral phase of PZNT91/09) on the electric field (E) applied in the same direction as the DC poling field using a photonic sensor. A large hysteresis regarding E vs strain appeared between 400 and 1500 V/mm, the E of which (1500 V/mm) is the coercive field to obtain giant k_{31} in PZNT91/09. The large hysteresis for E vs shrinkage strain corresponds to the large hysteresis for E vs expansion strain in PZNT91/09 single crystal. Therefore, it was found that the large hysteresis for E vs strain (shrinkage and expansion) is due to the generation of giant k_{31} .

Fig. 25. Applied field (E) dependence of shrinkage strain in the length (13 mm) direction in PZNT91/09 single-crystal plate with giant k_{31} .

Figure 26 shows the Ti composition (x) dependence of E vs strain in PMNT(1- x)/ x single-crystal plates measured at room temperature (pseudo-cubic phase) and under $E=1500$ V/mm. By increasing x from 0.251 to 0.299, the linear relationship between E and strain changed into a line with a brake, and finally reached to a typical E vs strain similarly to the case of PZT ceramics. Furthermore, the E of 800 V/mm to generate the triple and asymmetric loops corresponded to the E of a break in the line for E vs strain.

Fig. 26. Ti composition dependence (x) of E vs strain in PMNT(1- x)/ x single-crystal plates; $x=0.251$ (linear line and small hysteresis), $x=0.279/0.291$ (line with break and intermediate hysteresis) and $x=0.299$ (large hysteresis like PZT ceramics).

4.2.3 Field-induced phase transition

A mechanism to realize giant k_{31} can be explained using the crystal plane, which closely affects the direction of the spontaneous polarization, and poling direction. Giant k_{31} in relaxor single-crystal plates can be achieved when the poling field generates strain to move the ferroelectric domains in the plates ($13^L \times 4.0^W$ mm) and not to only expand the spontaneous polarization axes in the direction of the poling field. Figure 27 shows the relationships between crystal planes, spontaneous polarization axes, and poling direction in (110) PMNT(1- x)/ x single-crystal plates ($x=0.251-0.301$) in comparison with the case of (100) and (110) PZNT91/09 single-crystal plates. The crystal phases after poling can be estimated using the values of k_{31} and the combination between the directions of the spontaneous polarization axes and the poling field, which generates the strain to move the domains in the plates. Therefore, it was considered that the crystal phase of the PMNT(1- x)/ x single-crystal plates after poling changed from pseudo-cubic to pseudo-cubic ($x=0.251-0.262$) from pseudo-cubic to orthorhombic ($x=0.273-0.293$), and from pseudo-cubic to rhombohedral ($x=0.296-0.301$), because of the combination to move the domains in the plates. These results were supported by the fact that the shapes of the P-E loops are triple or asymmetrical. Furthermore, it was considered that the E for such types of loops to appear was a coercive field to generate the DC-field-induced phase transition with giant k_{31} .

In conclusion of this part, the relationships between giant k_{31} (>80%) and k_{33} (>90%) in (100) PZNT91/09 and (110) PMNT(1- x)/ x single-crystal plates were clarified to investigate the P-E hysteresis loops and the strain measurement. Triple and asymmetrical loops appeared in PMNT(1- x)/ x single-crystal plates with giant k_{31} as well as in PZNT91/09 single-crystal plates with giant k_{31} . The typical relaxor-type hysteresis was observed for the electric-field-induced strain and their break points correspond to the coercive field to generate giant k_{31} . The crystal

phases after DC poling could be estimated using the relationships between the crystal plane, which closely affects the direction of the spontaneous polarization, and poling direction.

Fig. 27. Schematic diagrams of relationships between crystal plane, which affects direction of spontaneous polarization, and poling direction for realizing giant k_{31} (>80%) in (110) PMNT(1-x)/x (pseudo-cubic phase before poling) and PZNT91/09 (rhombohedral phase before poling) single-crystal plates at poling temperature of 40 °C.

5. Applications

Utilizing the giant k_{31} and d_{31} in PZNT91/09 single crystals, devices such as piezoelectric unimorphs and bimorphs were fabricated in comparison with the devices consisting of PZT ceramics.

5.1 Applications of $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ single-crystal plates with giant k_{31} to piezoelectric unimorphs and bimorphs

In this part, the piezoelectric and displacement properties on various kinds of unimorphs and bimorphs were reported. Piezoelectric unimorphs were prepared by sticking the PZNT91/09 single-crystal plates with giant k_{31} on center shim plates ($15^{\text{L}} \times 4^{\text{W}} \times 0.10^{\text{T}} / 0.20^{\text{T}}$ mm) composed of 42 nickel alloy. These were compared with unimorphs fabricated by ordinary PZT ceramic plates ($k_{31}=37\%$, $d_{31}=-330$ pC/N) with the same dimensions. Furthermore, series-type bimorphs were made from the unimorphs by sticking other PZNT91/09 single-crystal plates and also PZT ceramic plates. The coupling factors on the bending mode (k_{b}) of the unimorphs and bimorphs were evaluated. The displacement of the devices was measured by laser displacement equipment at room temperature.

5.1.1 Realization of giant k_{31} over 80% in single-crystal plates

Table 4 shows the poling and annealing processes to obtain the giant k_{31} over 80%. When we poled three plate samples ($13^{\text{L}} \times 4^{\text{W}} \times 0.36^{\text{T}}$ mm) of Nos. 1~3, only the one sample of No. 3-1 had a giant k_{31} of 85.6%. The others were 42.2% (No. 1-1) and 40.4% (No. 2-1). Therefore, the

Sample No.	E (kV/mm)	k_{31} (%)	k_t (%)
1-1	1.0	42.2	55.1
	Annealing	0.0	0.0
1-2	1.0	49.6	59.0
1-3	1.5	39.6	55.8
1-4	2.0	79.5	56.2
1-5	2.5	55.7	59.6
1-6	3.0	39.8	55.7
2-1	1.0	40.4	54.9
	Annealing	0.0	0.0
2-2	1.0	45.4	54.2
2-3	1.5	86.2	56.2
3-1	1.0	85.6	56.8

Table 4. Process combination of poling and annealing to obtain Giant k_{31} .

annealing at 200 °C for 30 min was carried out to de-polarize the samples. On the following processes, the poling fields increased from 1.0 kV/mm to 3.0 kV/mm. As a result, the giant k_{31} was realized in the cases of No. 1-4 and No. 2-3 while the electromechanical coupling factors of the thickness mode (k_t) were almost the same of 54~60%. This means that the domain reorientation in thickness had been saturated; on the other hand, the one in the plate is changeable by the poling field. Furthermore, there was an optimum DC poling field for appearing the giant k_{31} on each individual plate sample. As mentioned above, the giant k_{31} can be obtained by the process combination of the DC poling and the annealing. Figure 28

Fig. 28. Frequency responses of impedance on k_{31} mode in (a) PZNT91/09 single-crystal plate and (b) PZT ceramic plate.

shows the comparison between frequency responses of impedance in (a) the PZNT91/09 single-crystal plate and (b) the conventional PZT ceramic plate. The k_{31} 's were 86.2% (PZNT91/09: sample No. 2-3 in Table 4) and 37.3% (PZT), respectively.

5.1.2 Bending mode properties

The PZNT91/09 single-crystal plate ($13^L \times 4.0^W \times 0.36^T$ mm) with giant k_{31} of 86.2% (No. 2-3 in Table 4) was stuck on a center shim plate ($15^L \times 4^W \times 0.20^T$ mm) composed of 42 nickel alloy to prepare a piezoelectric unimorph. The same dimensions of the PZT ceramic plate ($k_{31}=37\%$, $d_{31}=-330$ pC/N) was also used to realized a unimorph. Figure 29 shows the comparison between frequency responses of impedance in (a) the PZNT91/09 single-crystal unimorph and (b) the conventional PZT ceramic unimorph. The $k_b=64.7\%$ on bending mode in the PZNT91/09 single-crystal plate was three times larger than the $k_b=20.6\%$ in the PZT ceramic plate. Therefore, it was confirmed that the giant k_{31} and d_{31} constant could be useful to realize the piezoelectric unimorphs with high efficiency as well as the plate ($13^L \times 4.0^W \times 0.36^T$ mm) resonators with giant k_{31} and d_{31} constant.

Fig. 29. Frequency responses of impedance on k_b mode in (a) PZNT91/09 single-crystal unimorph and (b) PZT ceramic unimorph.

A piezoelectric bimorph was fabricated by sticking the PZNT91/09 single-crystal plate with giant k_{31} of 85.6% (No. 3-1 in Table 4) on the PZNT91/09 single-crystal unimorph with the k_b of 64.7% as previously mentioned. A PZT ceramic bimorph was also prepared. Figure 30 shows the comparison between frequency responses of impedance in (a) the PZNT91/09

single-crystal bimorph and (b) the conventional PZT ceramic bimorph. The $k_b=69.8\%$ on bending mode in the PZNT91/09 single-crystal plate was twice larger than $k_b=31.2\%$ in the PZT ceramic plate. Therefore, it was confirmed that highly efficiency piezoelectric devices could be realized to utilize PZNT91/09 single-crystal plates with giant k_{31} and d_{31} constant in the cases of the piezoelectric bimorphs as well as the piezoelectric unimorphs.

Fig. 30. Frequency responses of impedance on k_b mode in (a) PZNT91/09 single-crystal bimorph and (b) PZT ceramic bimorph.

5.1.3 Displacement properties

The displacement was evaluated regarding the PZNT91/09 single-crystal unimorphs (the center shim plate thickness of 0.20 mm)/ bimorphs (the center shim plate thickness of 0.10 mm) and the PZT ceramic unimorphs (the center shim plate thicknesses of 0.10 mm and 0.20 mm)/ bimorphs (the center shim plate thickness of 0.10 mm). In the case of a series-type bimorph in Fig. 31, the total displacement ($u=a+b$) was estimated by the following equation;

$$u = \left(\frac{3}{2} d_{31} \left(\frac{l}{t} \right)^2 \cdot \left(1 + \frac{t_s}{t} \right) V \alpha \right) \times 2 \quad (1)$$

where l : effective length (9 mm), t : thickness of devices (0.36+0.2 mm for single-crystal and ceramic unimorphs, 0.36+0.1 mm for ceramic unimorph, and 0.36x2+0.1 mm for single-

crystal and ceramic bimorphs), t_s : thickness of shim plate (0.1 mm and 0.2 mm), V : applied voltage and α : non-linearity coefficient, respectively.

Fig. 31. Series type bimorphs and total displacement.

The relationships between the applied voltage and the displacement were shown in Fig. 32 for the different shim thickness in the PZNT single-crystal unimorph and the PZT ceramic unimorph. The d_{31} constants of the stuck piezoelectric plates calculated from the frequency responses of the impedance were -2020 pC/N in the PZNT91/09 single crystal and -330 pC/N in the PZT ceramics, respectively. The displacement of the PZNT91/09 single-crystal unimorph was twice larger than the one of the PZT ceramic unimorph. The decrease in thickness of the shim plate from 0.20 mm to 0.10 mm increased the displacement in the range of over 100 V. The α calculated from (1) was 0.4~0.5 in the PZNT91/09 single-crystal unimorph. Otherwise, the α was 1.0 (≤ 100 V) and 1.6 at 180 V in the PZT ceramic unimorph. Furthermore, the α was independent of the shim plate thickness in the PZT ceramic unimorphs.

Fig. 32. Applied voltage dependence of displacement in PZNT91/09 single-crystal unimorph (□: shim thickness of 0.20 mm) and PZT ceramic unimorph (■: shim thicknesses of 0.20 mm and ♦ : 0.10 mm).

Figure 33 shows the applied voltage dependence of the displacement in the PZNT91/09 single-crystal bimorph and the PZT ceramic bimorph. The average d_{31} constants of the two stuck PZNT91/09 single-crystal plates and the two stuck PZT ceramic plates also showed in this figure. Although the d_{31} constant of the PZNT91/09 single crystals is 4~7 times larger than the d_{31} of the PZT ceramics, the displacement of the PZNT91/09 single-crystal bimorph became almost twice larger than the one of the PZT ceramic bimorph. The reason the displacement becomes twice, not more, was due to that the α in the PZNT91/09 single-crystal bimorph was a half of the α in the PZT ceramic bimorph.

Fig. 33. Applied voltage dependence of displacement in PZNT91/09 single-crystal bimorph (○: shim thickness of 0.10 mm) and PZT ceramic bimorph (●: shim thickness of 0.10 mm).

The origin of the decrease in α of the PZNT91/09 single-crystal bimorph was thought the mechanical softness of PZNT91/09 single-crystal plates with giant k_{31} and d_{31} constant. Namely, the Young's modulus of PZNT single crystals (0.89×10^{10} N/m) is one order smaller than the one of PZT ceramics ($6 \sim 8 \times 10^{10}$ N/mm). In addition to the above mentioned, the values of α in bimorphs were approximately twice larger than the ones of unimorphs. This phenomenon was thought that the α depends on the number of the piezoelectric plate; one plate in unimorph and two plates in bimorph, respectively.

In conclusion of this part, the process combination of poling and annealing to obtain giant k_{31} and d_{31} constant was clarified to fabricate PZNT91/09 single-crystal unimorphs and bimorphs. The coupling factors on bending mode (k_b) in PZNT91/09 single crystal unimorphs and bimorphs were 2~3 times larger than the k_b 's in PZT ceramic unimorphs and bimorphs. The displacement of PZNT91/09 single-crystal unimorphs and bimorphs was almost twice larger than the one of PZT ceramic devices. The advantage of PZNT91/09 single-crystal plates with giant k_{31} and d_{31} constant was confirmed through the development of piezoelectric devices such as unimorphs and bimorphs.

6. Conclusion

We found the giant electromechanical coupling factor of k_{31} mode to be over 80% and the piezoelectric d_{31} constant to be nearly -2000 pC/N in ferroelectric relaxor single-crystal plates. The discovery of the giant k_{31} and the d_{31} constant became breakthroughs in applications to high-performance sensors and actuators utilizing k_{31} mode.

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Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on the application of ferroelectric devices to innovative systems. In particular, the use of these materials as varying capacitors, gyroscope, acoustics sensors and actuators, microgenerators and memory devices will be exposed, providing an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric devices.

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