

Enhanced Piezoelectric Properties of Lead-free Piezoelectric Materials by Domain Engineering

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For the [111] poled barium titanate (BaTiO_3) single crystals with the engineered domain configuration, it was clearly observed that the piezoelectric properties increased with decreasing domain sizes. To explain the phenomenon, the multidomain single crystals were regarded as the composite of (a) a distorted domain wall region and (b) a normal tetragonal domain region. Using a 2-phases model, the piezoelectric properties from the domain wall were estimated. As a result, ultrahigh piezoelectric constants over 8,000 pC/N were expected from the domain wall region. Moreover, this study suggested that it is possible to obtain the lead-free piezoelectric materials with the d_{31} and d_{33} over 1,000 pC/N, when the domain sizes can decrease below 1 μm .

Key words: barium titanate, engineered domain configuration, domain engineering, piezoelectric property

1. INTRODUCTION

Recently, lead-free ferroelectrics have become highly attractive materials from the viewpoint of a solution to environmental problems.¹⁾ However, as compared with $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) ceramics,²⁾ their ferroelectric related properties were very poor, and therefore it is difficult to replace the PZT ceramics. Many researchers have attempted to improve the piezoelectric properties of lead-free ferroelectrics such as bismuth layer-structure ferroelectrics, BaTiO_3 and potassium niobate (KNbO_3) by chemical modification, but no significant improvement has been achieved.¹⁻³⁾ Recently, however, chemically modified KNbO_3 and Sodium niobate (NaNbO_3) solid solution ceramics were reported as new lead-free piezoelectrics with the similar piezoelectric properties to PZT ceramics.⁴⁾ Thus, there are still some possibilities to obtain high performance lead-free piezoelectrics by the chemical modification. On the other hand, there is also a possibility that a new ferroelectrics with a new chemical formula can show a high piezoelectric performance, but although it took over 50 years after discovery of BaTiO_3 , there is no new ferroelectrics with high piezoelectric properties.

To achieve much higher piezoelectric properties than those of PZT ceramics, the domain engineering technique should be applied to lead-free ferroelectric materials. Domain engineering is an important technique for obtaining enhanced piezoelectric properties in ferroelectric single crystals. In [001] oriented rhombohedral $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) – lead titanate ($\text{PbTiO}_3 = \text{PT}$) single crystals, ultrahigh piezoelectric activities were found by Park and Shrout⁵⁾ and Kuwata *et al.*⁶⁾ and these ultrahigh piezoelectric properties were originated from the application of the domain engineering techniques, *i.e.*, engineered domain configuration.⁷⁻⁹⁾

BaTiO_3 crystal is a typical lead-free ferroelectrics and there have been a number of reports on its domain engineering.⁹⁻¹¹⁾ Park *et al.*¹¹⁾ reported that the [001] poled orthorhombic BaTiO_3 crystals with the engineered

domain configurations exhibited d_{33} of over 500 pC/N and k_{33} of over 85%. These piezoelectric properties are much higher than those of "soft" PZT ceramics.²⁾ Moreover, for the tetragonal BaTiO_3 crystals with the engineered domain configurations, it was recently found that the piezoelectric properties significantly improved with decreasing domain sizes.⁹⁾ These results suggested that the domain walls in the engineered domain configuration could contribute significantly to the piezoelectric properties.

The objective in this study is to explain the domain size dependence of the piezoelectric properties for the BaTiO_3 crystals with engineered domain configurations. For this objective, the piezoelectric properties of the BaTiO_3 crystals were investigated as a function of domain size. Finally, the effect of 90° domain walls on the piezoelectric properties was discussed.

2. EXPERIMENTAL

BaTiO_3 single crystals were grown by a TSSG method at Fujikura, Ltd.¹²⁾ These crystals were oriented along [111] direction using a back-reflection Laue method. For the piezoelectric measurement using the 31 resonators, BaTiO_3 single crystals were sized into $4.0 \times 1.2 \times 0.4 \text{ mm}^3$ ($4.0 \text{ mm} // [1-10]$, $1.2 \text{ mm} // [11-2]$, $0.4 \text{ mm} // [111]$) by cutting and polishing using fine Al_2O_3 powders. Gold electrodes were sputtered on both sides ($4.0 \times 1.2 \text{ mm}^2$). Poling treatment for the preparation of BaTiO_3 crystals with different domain sizes was performed on the basis of the previous reports of domain size dependence on the electric-fields and the temperatures.⁹⁾

On the other hand, for the piezoelectric measurement using the 33 resonators, the BaTiO_3 single crystals were sized into $0.8 \times 0.8 \times 2.0 \text{ mm}^3$ ($0.8 \text{ mm} // [1-10]$, $0.8 \text{ mm} // [11-2]$, $2.0 \text{ mm} // [111]$) by cutting and polishing. Gold electrodes were sputtered on both sides ($0.8 \times 0.8 \text{ mm}^2$). The BaTiO_3 crystals were set in the micro silicone-oil bath on the heater of cryostat, and the various electric-fields were applied just above Curie temperature.

After the poling treatment, their domain configurations

of the both resonators were investigated using the polarizing microscope (Nikon, Labphoto2-POL). Finally, their piezoelectric properties were measured using an impedance analyzer (Agilent, HP-4294A) by a conventional resonance-antiresonance method¹³⁾.

3. RESULT AND DISCUSSION

3.1 Domain size dependence of piezoelectric properties using the 31 resonators

By the poling treatment at the similar electric-fields and temperatures reported for BaTiO₃,⁹⁾ the 31 resonators of BaTiO₃ crystals with different domain sizes were prepared. The average domain sizes in the engineered domain configuration were changed from 40 μm to 5.5 μm. The domain configurations for all resonators prepared in this study were composed of the same 90° domain walls,¹⁴⁾ and the difference between these domain configurations was just domain size, i.e., domain wall density.

These piezoelectric properties were measured at 25 °C using a weak AC electric-field of 125 mV/mm. Table I shows the domain size dependence of piezoelectric-related properties using these 31 resonators. As a reference, a calculated d₃₁ piezoelectric constant for [111] oriented BaTiO₃ single-domain crystal using the material constants reported by Zgonik *et al.*¹⁵⁾ was also listed. With decreasing domain size, all piezoelectric-related properties increased significantly. Especially, the 31 resonator with a domain size of 5.5 μm showed much higher d₃₁ of -230 pC/N and k₃₁ of 47.5 % than those (d₃₁ of -171 pC/N and k₃₁ of 34.4 %) reported for soft PZT ceramics.²⁾

To date, it was considered that the highest piezoelectric property must be obtained for the single-domain crystals, and it is impossible for the material constants to be beyond the single-domain crystals' values. However, this study revealed that the 90° domain walls in the engineered domain configuration significantly contributed to piezoelectric-related properties, and caused much higher values than those from single-domain crystals.

In general, under the high electric-field exposure, the domain walls can move very easily, and this domain wall motion made an intrinsic contribution of the domain walls themselves to the piezoelectric properties very unclear. However, in the engineered domain configuration, it should

Table I. Piezoelectric properties of the BaTiO₃ single crystals poled along [111] direction using the 31 resonators.

BaTiO ₃ single crystals	ϵ_{33}^T	S_{11}^E (pm ² /N)	d_{31} (pC/N)	k_{31} (%)
[001] ^{a)} (single-domain)	129	7.4	-33.4	—
[111] ^{b)} (single-domain)	---	---	-62.0	---
[111], charged (domain size of 40 μm)	2,185	7.37	-97.8	25.9
[111], charged + neutral (domain size of 13.3 μm)	2,087	7.68	-134.7	35.7
[111], charged + neutral (domain size of 6.5 μm)	2,441	8.80	-180.1	41.4
[111], charged + neutral (domain size of 5.5 μm)	2,762	9.58	-230.0	47.5
"soft" PZT ceramics ^{c)} Pb _{0.988} (Ti _{0.48} Zr _{0.52}) _{0.978} Nb _{0.022} O ₃	1,700	16.4	-171.0	34.4

a): measured by Zgonik *et al.*

b): calculated using the values measured by Zgonik *et al.*

c): measured by Inffe *et al.*

be noted that the 90° domain walls cannot move with and without unipolar DC electric-field exposure.^{10,11)} This means that in the engineered domain configuration, the 90° domain walls can exist very stably with and without unipolar electric-field exposure. Therefore, the intrinsic contribution of the domain walls to the piezoelectric properties was clarified for the first time using the engineered domain configuration. On the other words, the engineered domain configuration can be considered as a domain-wall engineering among the domain engineering techniques.¹⁶⁾

3.2 Domain size dependence of piezoelectric properties using the 33 resonators

By the poling treatment at various electric-fields and temperatures,⁹⁾ the 33 resonators of BaTiO₃ crystals with different domain sizes were prepared. The average domain sizes in the engineered domain configuration were changed from 100 μm to 14 μm. For the 31 resonator, minimum domain size was 5.5 μm while for the 33 resonator, minimum domain size was 14 μm. This difference caused from the difference of applied electric-field. This is because that in this study, domain sizes decreased with increasing applied electric-fields. The domain configurations for all resonators prepared in this study were composed of the same 90° domain walls,¹⁴⁾ and the difference between these domain configurations was just domain size.

These piezoelectric properties were measured at 25 °C using a weak AC electric-field of 50 mV/mm. Table II shows the domain size dependence of piezoelectric-related properties using these 33 resonators. As a reference, a calculated d₃₃ piezoelectric constant for [111] oriented BaTiO₃ single-domain crystal using the material constants reported by Zgonik *et al.*¹⁵⁾ was also listed. With decreasing domain size, all piezoelectric-related properties increased. However, for the 33 resonators, with decreasing domain sizes, the enhancement of piezoelectric properties was not so large. Now, we cannot explain this difference between the 31 and 33 resonators, but it may be originated from the difference of these domain configurations.

3.3 Calculation of piezoelectric properties contributed from the 90° domain walls

It is well known that a region near the 90° domain walls is gradually distorted to relax the strain between domains with different polar directions. Moreover, for BaTiO₃ crystals, the crystal structure near the 90° domain walls

Table II. Piezoelectric properties of the BaTiO₃ single crystals poled along [111] direction using the 33 resonators.

BaTiO ₃ single crystals	ϵ_{33}^T	S_{33}^E (pm ² /N)	d_{33} (pC/N)	k_{33} (%)
[111] ^{a)} (single-domain)	---	---	224	---
[111], neutral (domain size of 100 μm)	1,959	10.7	241	55.9
[111], neutral (domain size of 22 μm)	2,008	8.8	256	64.7
[111], neutral (domain size of 14 μm)	1,962	10.8	289	66.7

a): calculated using the values measured by Zgonik *et al.*

gradually changed from normal tetragonal with c/a ratio of 1.011 to tetragonal with c/a ratios closed to 1.0. Thus, it can be expected that the region near the 90° domain walls with pseudo-cubic structure exhibits the material constants of BaTiO_3 single crystals near the Curie temperature as reported by Budimir *et al.*¹⁷⁾ In this study, the BaTiO_3 crystals with the engineered domain configuration were regarded as a composite of (a) normal tetragonal region and (b) distorted domain wall region. On the basis of this 2-phases model, a volume fraction of the distorted domain wall region on the normal tetragonal region was estimated as follows. For a simplification of calculation, one dimensional model was applied.¹⁸⁾ First, a thickness of the distorted 90° domain wall region was assumed using various sizes from 1 to 100 nm.¹⁷⁻²¹⁾ Next, using this thickness of the distorted 90° domain wall region (W_{DW}) and the domain size (W_D), the volume fraction of the distorted 90° domain wall region (F) was estimated using the following equation,

$$F = \frac{W_{DW}}{W_D} \quad (1).$$

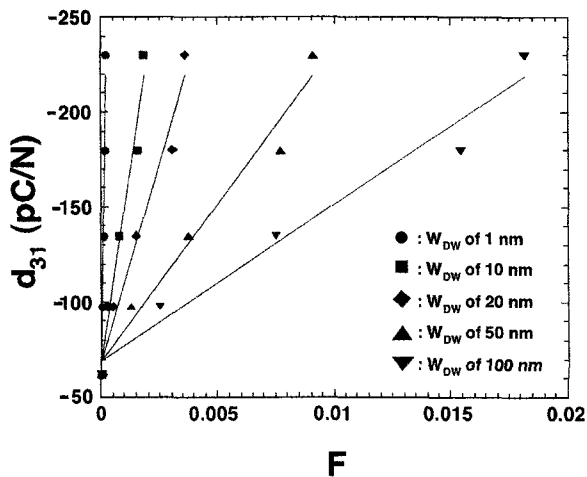


Fig. 1 Relationship between d_{31} and F calculated using various W_{DW} from 1 to 100 nm.

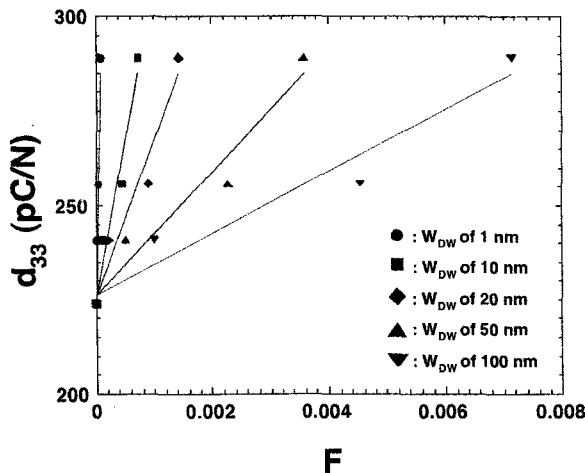


Fig. 2 Relationship between d_{33} and F calculated using various W_{DW} from 1 to 100 nm.

W_D can be measured from the experiment in this study while W_{DW} is unknown values. Thus, we must use valid W_{DW} values for the above calculation. To date, many researchers tried to clarify the domain wall thickness using LGD theories and TEM observation, and their estimated values are distributed from 1 to 100 nm.¹⁷⁻²¹⁾ Recently, with developing measurement equipments and theories, some new methods were proposed to estimate the domain wall thickness.¹⁹⁻²¹⁾ Chaib *et al.* estimated the 90° domain wall thickness of 12 nm for BaTiO_3 using the quantum mechanical method.¹⁹⁾ Shilo *et al.* measured the 90° domain wall thickness from 1 to 10 nm for PbTiO_3 using atomic force microscopy.²⁰⁾ On the other hand, Tsuji *et al.* measured the 90° domain wall thickness of around 20 nm for PZT ceramics using ultrasonic atomic force microscopy.²¹⁾ Moreover, the domain wall thickness was related to point defect, and the defect was responsible for the broadening of the domain wall thickness.²⁰⁾ This means that it is very difficult to determine the 90° domain wall thickness for BaTiO_3 . Thus, in this study, F values were calculated using the various domain wall thickness from 1 to 100 nm. Using the F values, the relationship between d_{31} and F was plotted in Fig. 1 while that between d_{33} and F was also plotted in Fig. 2. In Figs. 1 and 2, a slope of the line means the piezoelectric constants expected from the distorted 90° domain wall region. If the 90° domain wall thickness can be estimated as 10 nm, d_{31} and d_{33} was expressed using the following equation, respectively,

$$d_{31} = 82676 * F + 69 \quad (2),$$

$$d_{33} = 81744 * F + 227 \quad (3).$$

This suggested that if the 90° domain wall thickness is 10 nm, d_{31} and d_{33} from the distorted 90° domain wall region can be estimated as 82,676 and 81,744 pC/N, respectively. On the other hand, if the 90° domain wall thickness is 20 nm, d_{31} and d_{33} from the distorted 90° domain wall region can be also estimated as 41,338 and 40,872 pC/N, respectively. Moreover, if the 90° domain wall thickness is 100 nm, d_{31} of 8,268 and d_{33} of 8,174 can be expected from the distorted 90° domain wall region. The above discussion revealed that the piezoelectric constants expected from the distorted 90° domain wall region are significantly high (over 8,000 pC/N as a minimum value).

This study showed that the distorted 90° domain walls can contribute significantly to the piezoelectric properties. When the domain wall density increases more and more, what piezoelectric constants we can expect? The domain size dependence of d_{31} and d_{33} can be also expressed as follows,

$$d_{31} = \frac{826760}{W_D} + 69 \quad (4),$$

$$d_{33} = \frac{817440}{W_D} + 227 \quad (5).$$

It should be noted that these equations (4) and (5) are independent of W_{DW} . Thus, using the various W_D values, the relationship between d_{31} and W_D was plotted in Fig. 3 while that between d_{33} and W_D was also plotted in Fig. 4.

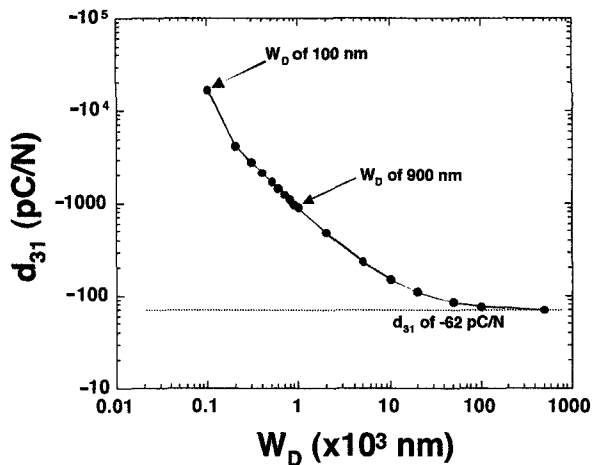


Fig. 3 Relationship between d_{31} and W_D calculated using the equation (4).

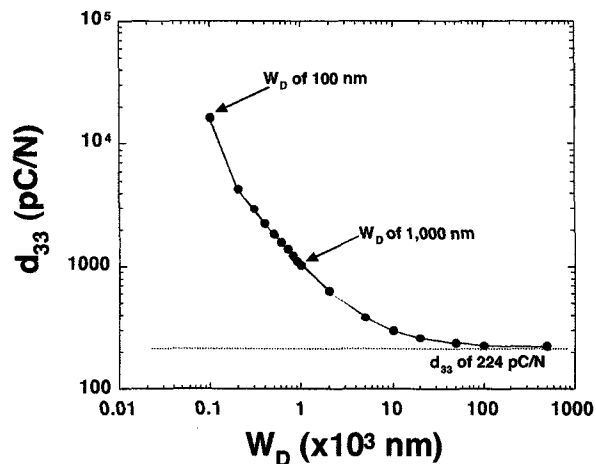


Fig. 4 Relationship between d_{33} and W_D calculated using the equation (5).

In Figs. 3 and 4, above the W_D of 20 μm , piezoelectric constants were almost constant at the calculated single-domain's values while below the W_D of 10 μm , piezoelectric constants drastically increased with decreasing domain sizes. Moreover, when the domain size decreased down to 1 μm , both d_{31} and d_{33} became to around 1,000 pC/N.

Park and Shrout reported that [001] poled PZN single crystal exhibited the ultrahigh d_{33} of 1,100 pC/N,²²⁾ and the domain size in this PZN crystal was observed at around 1 μm .⁷⁾ They also reported that for [111] poled PZN single-domain crystal had the d_{33} of just 83 pC/N²²⁾ similar to that of BaTiO₃. Therefore, it can be expected that when the domain size of around 1 μm is induced into the [111] poled BaTiO₃ crystals, high performance lead-free piezoelectrics with ultrahigh piezoelectric constants over 1,000 pC/N can be created.

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