

Enhanced Ferroelectric Related Behaviors of Ferroelectric Single Crystals using the Domain Engineering

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Domain engineering is very important technique to obtain the enhanced piezoelectric and ferroelectric related properties for ferroelectric single crystals. One of the domain engineering techniques is the engineered domain configurations. This domain technique uses anisotropy of ferroelectric single crystals as a function of crystallographic orientation. For example, if rhombohedral crystal (polar direction of [111]) is used, the direction for the use of the engineered domain is [100] direction. In fact, rhombohedral $\text{Pb}(\text{Zn}_{1-x}\text{Nb}_{2x})\text{O}_3$ - PbTiO_3 (PZN-PT) crystals with the applied E-field along [100] direction showed ultralarge strain ($d_{33} > 2,500$ pC/N) and high electromechanical coupling factors ($k_{33} > 90$ %). On the other hand, the rhombohedral PZN-PT crystals with the applied E-field along [111] direction showed poor d_{33} and k_{33} . Moreover, the crystal structures are also important factor for the engineered domain configurations. For example, the orthorhombic phase in barium titanate (BaTiO_3) single crystals exhibited the much higher ferroelectric related properties than the other phases such as tetragonal and rhombohedral phases. The relationship between the crystal structures and the crystallographic orientations were discussed.

Key word: domain engineering, piezoelectric property, barium titanate, crystallographic orientation, electric-field induced phase transition

1. INTRODUCTION

Domain engineering is very important technique to obtain the enhanced piezoelectric and ferroelectric related properties for ferroelectric single crystals. It is well known that recently, in [001] oriented rhombohedral PZN-PT single crystals, ultrahigh piezoelectric activities were found by Park *et al.*^{1,4)} and Kuwata *et al.*^{5,6)} with the strain over 1.7 %, the piezoelectric constant d_{33} over 2,500 pC/N, the electromechanical coupling factor k_{33} over 90 % and the hysteresis-free strain vs electric-field behavior. This ultrahigh piezoelectric properties were originated from one of the domain engineering techniques, *i.e.*, "the engineered domain configurations".

The engineered domain configuration is expected to possess the following three features for the excellent piezoelectric performance: (1) hysteresis-free strain vs electric-field behavior owing to inhibition of the domain wall motion, (2) higher piezoelectric constant along the non-polar direction owing to the tilt of polar vector by electric-field, and (3) change of the macroscopic symmetry in crystals with engineered domain configuration.^{7,8)} Therefore, if the concept of the engineered domain configuration can be applied to other ferroelectric single crystals, enhanced piezoelectric properties are expected.

This engineered domain configuration technique uses the anisotropy of the ferroelectric single crystals as a function of the crystallographic orientation. For example, if the rhombohedral ferroelectric crystal (polar direction of [111] direction) is used, the applied electric-field direction for the use of the engineered domain is [100] and [110] directions as shown in Fig. 1. If the monoclinic ferroelectric crystal (polar direction of [110] direction) is used, the applied electric-field

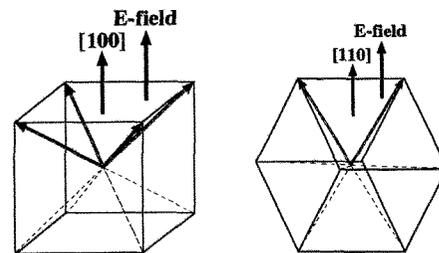


Fig. 1 Schematic model of the engineered domain configurations for the rhombohedral ferroelectric single crystals.

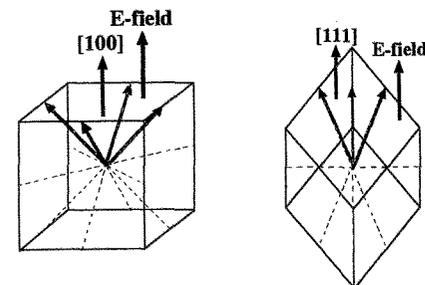


Fig. 2 Schematic model of the engineered domain configurations for the monoclinic ferroelectric single crystals.

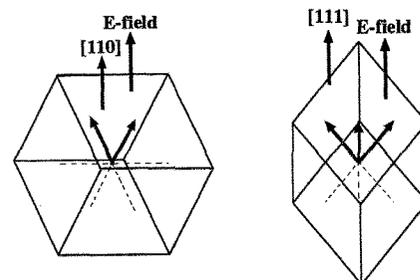


Fig. 3 Schematic model of the engineered domain configurations for the tetragonal ferroelectric single crystals.

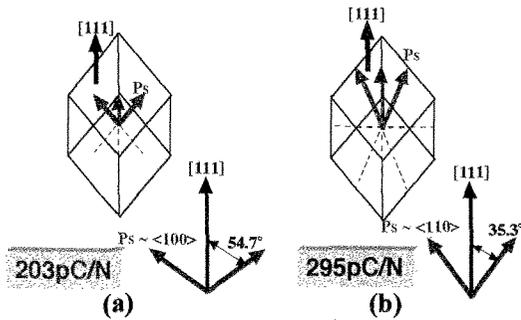


Fig. 4 Two engineered domain configurations for the [111] poled (a) tetragonal and (b) monoclinic BaTiO₃ single crystals.

direction for the use of the engineered domain is [100] and [111] directions as shown in Fig. 2. Moreover, if the tetragonal ferroelectric crystal (polar direction of [001] direction) is used, the applied electric-field direction for the use of the engineered domain is [111] and [110] directions as shown in Fig. 3. As the above mentioned, the rhombohedral PZN-PT crystals with the applied electric-field along [001] direction showed ultralarge d_{33} over 2,500 pC/N and ultrahigh k_{33} over 90%. On the other hand, the rhombohedral PZN-PT crystals with the applied electric-field along [111] direction showed poor d_{33} and k_{33} .^{7, 8} Moreover, the crystal structures are also important factor for the engineered domain configurations.

BaTiO₃ single crystals have the tetragonal phase at room temperature. Thus, the piezoelectric properties were investigated using the [111] oriented tetragonal BaTiO₃ single crystals, as shown in Fig. 3.⁹

¹⁰ As the results, two kinds of the engineered domain configurations were formed, i.e., (1) the [111] poled tetragonal engineered domain and (2) the [111] poled monoclinic engineered domain. The former d_{33} was 203 pC/N while the latter d_{33} was 295 pC/N. This

is because for the tetragonal BaTiO₃ crystals, the higher electric-field exposure over 10 kV/cm along [111] direction led to the electric-field induced phase transition from tetragonal to monoclinic phases. It is known that the d_{33} value of the [001] poled tetragonal BaTiO₃ single crystals was 90 pC/N.¹² Therefore, the d_{33} of the [111] poled tetragonal BaTiO₃ was almost twice larger than that of the [001] poled tetragonal BaTiO₃, while that of the [111] poled monoclinic BaTiO₃ was almost three times larger than that of the [001] poled tetragonal BaTiO₃.

We must consider about this difference between 203 and 295 pC/N. Figure 4 shows two kinds of the engineered domain configurations for the [111] poled (a) tetragonal and (b) monoclinic BaTiO₃ single crystals. The both engineered domains were composed of three kinds of domains while the angle θ between the polar direction and the electric-field direction was quite different, i.e., d_{33} of 203 pC/N at θ of 54.7° while d_{33} of 295 pC/N at θ of 35.3°. Therefore, it is very important to clear whether this angle θ is very effective for the piezoelectric performance or not.

In this study, the piezoelectric properties of BaTiO₃ single crystals were investigated as a function of the crystallographic orientations ([001] and [111] directions), and the crystal structures (tetragonal, monoclinic and rhombohedral phases), as shown in Fig. 5. Moreover, the relationship between the crystal structures and the crystallographic orientations were also discussed.

2. EXPERIMENTAL

2.1 Growth of BaTiO₃ single crystals

BaTiO₃ single crystals were prepared by a top-seeded solution growth (TSSG) method at Fujikura, Ltd. The details of preparation of BaTiO₃ single

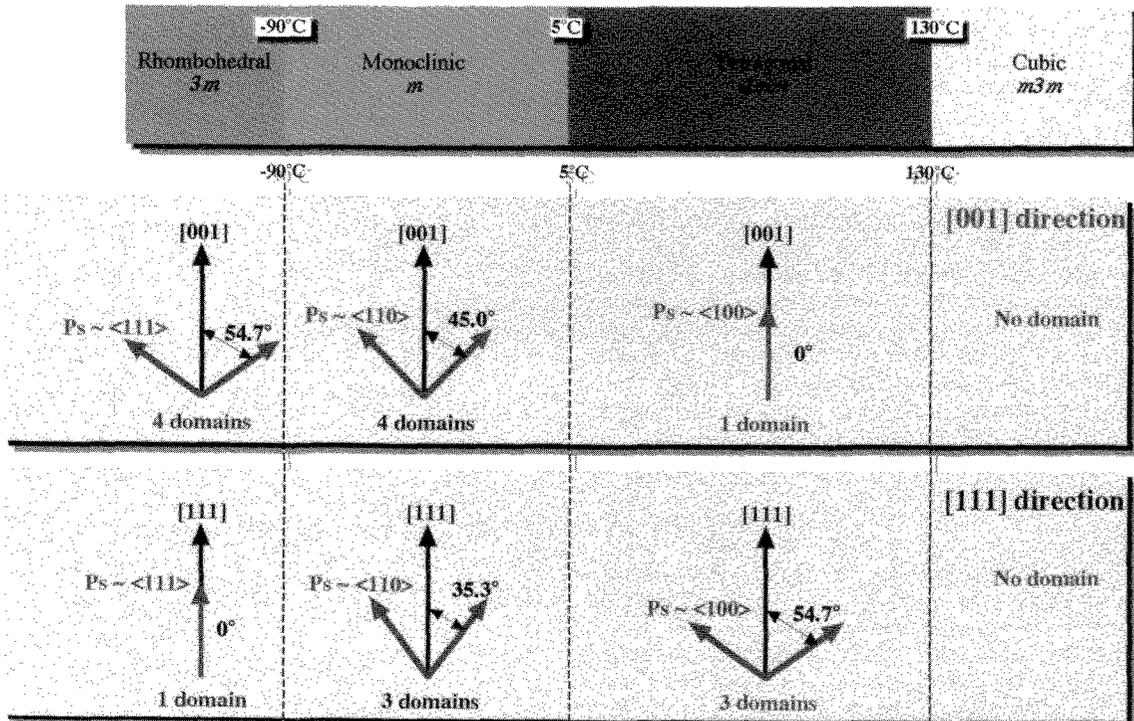


Fig. 5 Expected domain configurations for the [111] and [001] poled BaTiO₃ single crystals with three kinds of crystal structures.

crystals and their characterization were described elsewhere.¹³⁻¹⁶ These crystals were oriented along [001] and [111] directions using the back-reflection Laue method.

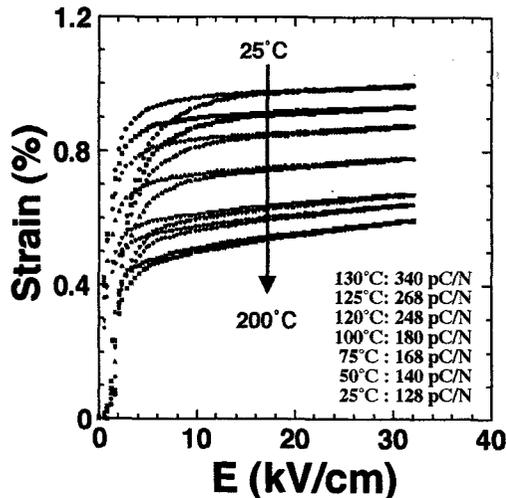


Fig. 6 Strain vs electric-field behaviors of the [001] oriented BaTiO₃ single crystals from 25 °C to 200 °C.

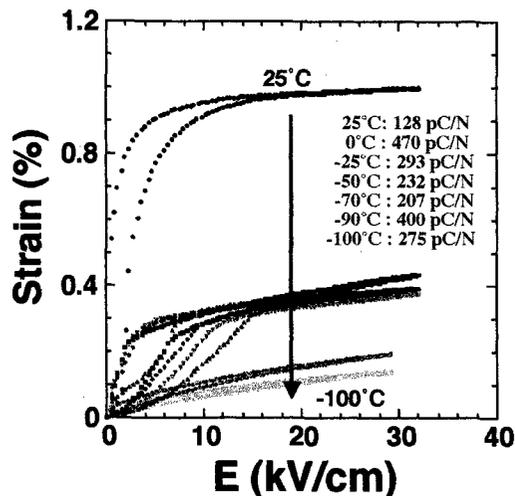


Fig. 7 Strain vs electric-field behaviors of the [001] oriented BaTiO₃ single crystals from 25 °C to -100 °C.

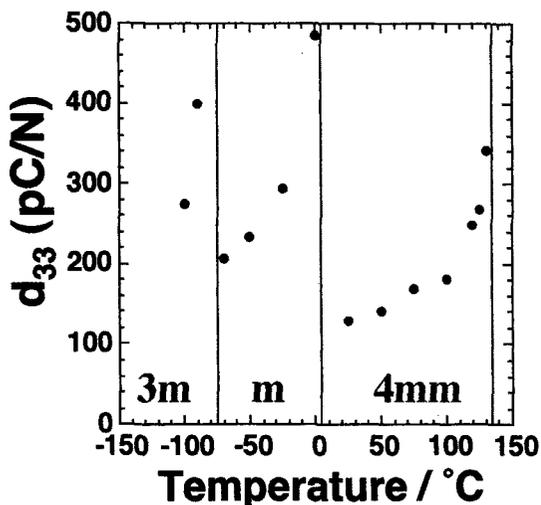


Fig. 8 The d_{33} vs temperature curve of the [001] oriented BaTiO₃ single crystals from -100 °C to 200 °C.

2.2 Piezoelectric measurement

For the high-field electrical measurement, the crystals were polished to achieve flat and parallel surfaces onto which gold electrodes were sputtered. Prior to piezoelectric measurements, the dielectric properties were measured with a LCR meter (HP4263A) at room temperature, and it was confirmed that their dielectric loss was below 0.1 % at 100Hz. High electric field measurements included polarization and strain using a modified Sawyer-Tower circuit and a linear variable differential transducer (LVDT) driven by a lock-in amplifier (Stanford Res. Sys., model SR830). Electric fields were applied using an amplified triangular waveform at 0.1Hz, using a Kepco BOP-1000M high-voltage DC amplifier (<1kV) and a Trek 609C-6 high-voltage DC amplifier (≥ 1 kV).

For the low-field electrical measurement using the IEEE resonance technique¹⁷⁾, two kinds of the crystals were prepared, with the shapes and the sizes for the k_{33} and k_{31} vibration modes. Low temperature properties under a DC bias were measured using an impedance analyzer (HP4194) in conjunction with a computer-controlled temperature chamber and a DC bias blocking circuit with a maximum capacity of 1 kV. For piezoelectric constants (d_{33}) determination of the k_{33} mode, the bar-shape crystal of 0.4x0.4x1.6 mm in length were prepared.

3. RESULTS AND DISCUSSION

3.1 High electric-field piezoelectric measurements

3.1.1 [001] oriented BaTiO₃ single crystals: Under the high electric-fields, the strain vs electric-field curves of the [001] oriented BaTiO₃ single crystals were measured from -100 °C to 200 °C, as shown in Figs. 6 and 7. On the basis of the slope of the strain behaviors over 20 kV/cm, the piezoelectric constant d_{33} was estimated directly, as shown in Fig. 8. It should be noted that for the [001] oriented monoclinic BaTiO₃ single crystals at 0 °C, the maximum d_{33} of 470 pC/N was obtained. This 470 pC/N was very large values, and almost comparable to that of PZT ceramics. From Fig. 8, the d_{33} of the [001] poled monoclinic BaTiO₃ single crystals was much higher than that of the [001] poled rhombohedral BaTiO₃ single crystals. In Fig. 5, when the electric-field was applied along [001] direction, two kinds of the engineered domain configurations could be formed, *i.e.*, (1) the [001] poled monoclinic BaTiO₃ crystal with 4 equivalent domains and θ of 45.0° and (2) the [001] poled rhombohedral BaTiO₃ crystal with 4 equivalent domains and θ of 54.7°. In the objective of this study, we expected that if the number of the equivalent domains constructing the engineered domain is same, the smaller angle θ can cause the larger piezoelectric properties. The result in Fig. 8 supported the above hypothesis. Therefore, when the electric-field was applied along [001] direction of BaTiO₃ single crystals, the monoclinic phase was very important for the higher piezoelectric performance.

3.1.2 [111] oriented BaTiO₃ single crystals: The strain vs electric-field curves of the [111] oriented BaTiO₃ single crystals were measured from -100 °C to 200 °C, as shown in Figs. 9 and 10. On the basis of the slope of the strain behaviors over 20 kV/cm, the piezoelectric constant d_{33} was estimated directly, as

shown in Fig. 11. In Figs. 9 and 10, the strain vs electric-field curves at 25 °C exhibited the discontinuous behaviors owing to the two kinds of the electric-field induced phase transitions, *i.e.*, (1)

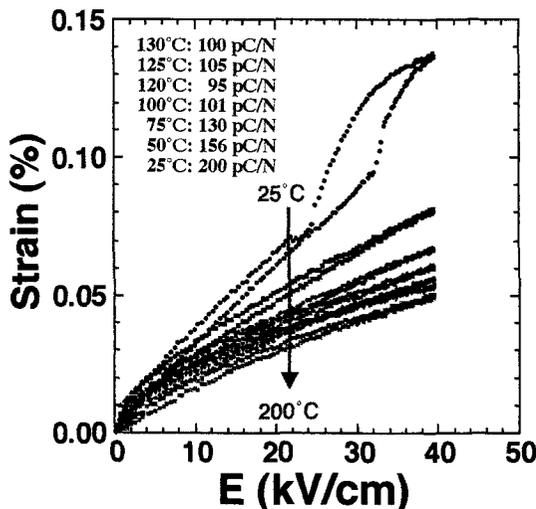


Fig. 9 Strain vs electric-field behaviors of the [111] oriented BaTiO₃ single crystals from 25 °C to 200 °C.

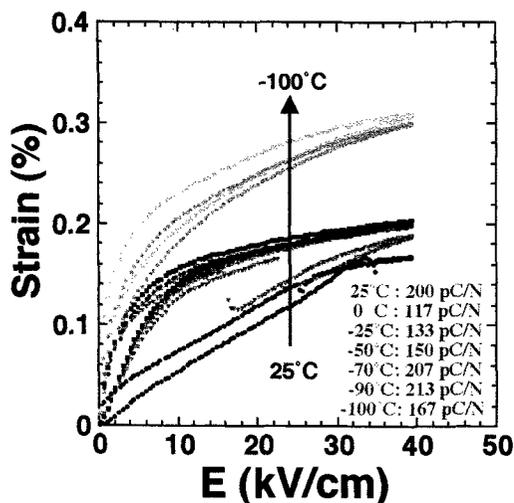


Fig. 10 Strain vs electric-field behaviors of the [111] oriented BaTiO₃ single crystals from 25 °C to -100 °C.

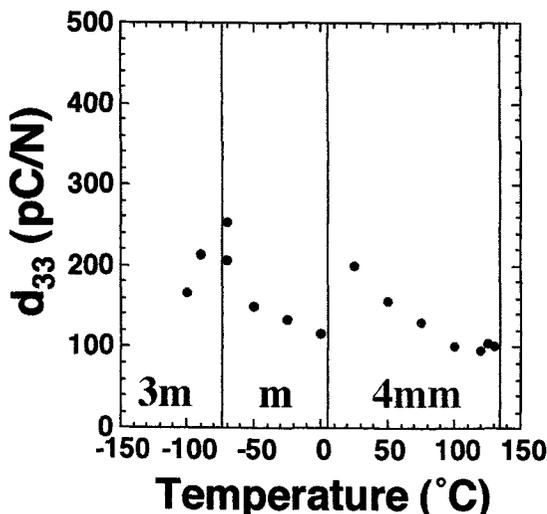


Fig. 11 The d_{33} vs temperature curve of the [111] oriented BaTiO₃ single crystals from -100 °C to 200 °C.

the 1st transition from tetragonal to monoclinic phase around 4-6 kV/cm and (2) the 2nd transition from monoclinic to rhombohedral phase around 30 kV/cm.^{9,10} In Fig. 11, it should be noted that for the [111] oriented monoclinic BaTiO₃ single crystals at -70 °C, the maximum d_{33} of 260 pC/N was obtained. As the above mentioned, the d_{33} of the [111] poled monoclinic BaTiO₃ crystal at 25 °C was 295 pC/N (Fig. 4). On the other hand, the d_{33} of the [111] poled monoclinic BaTiO₃ crystal at -70 °C was 260 pC/N (Fig. 11). Now, we believe that this difference may be caused by the change of the temperature. Moreover, in Fig. 11, the d_{33} of the [111] poled monoclinic BaTiO₃ single crystals was much higher than that of the [111] poled tetragonal BaTiO₃ single crystals. In Fig. 5, when the electric-field was applied along [111] direction, two kinds of the engineered domain configurations could be formed, *i.e.*, (1) the [111] poled monoclinic BaTiO₃ crystal with 3 equivalent domains and θ of 35.3° and (2) the [111] poled tetragonal BaTiO₃ crystal with 3 equivalent domains and θ of 54.7°. Therefore, it was confirmed that when the number of the equivalent domains constructing the engineered domain is same, the smaller angle θ can cause the larger piezoelectric properties. Therefore, when the electric-field was applied along [111] direction of BaTiO₃ single crystals, the monoclinic phase was also very important for the higher piezoelectric performance.

3.1.3 Expectation of the best engineered domain configuration in BaTiO₃ single crystals: The above discussions suggested that as the factors which can be responsible for the piezoelectric performance, there were two ones, *i.e.*, (1) the number of the equivalent domains constructing the engineered domain and (2) the angle θ between the polar direction and the electric-field direction. Considering about Fig. 5, we will check the piezoelectric constants in Figs. 8 and 11. As the above mentioned, when the number of the equivalent domains constructing the engineered domain was same, the smaller angle θ caused the larger piezoelectric properties. Next, the role of the number of the equivalent domains constructing the engineered domain was also discussed. The [001] poled rhombohedral BaTiO₃ crystal had 4 equivalent domains and θ of 54.7° while the [111] poled tetragonal BaTiO₃ crystal had 3 equivalent domains and θ of 54.7°. Thus, This comparison between two engineered domains can give us the information about the role of the number of the equivalent domains constructing the engineered domain under the same θ of 54.7°. The d_{33} of the [001] poled rhombohedral BaTiO₃ crystal was about 400 pC/N while that of the [111] poled tetragonal BaTiO₃ crystal was about 200 pC/N, *i.e.*, d_{33} of the [001] poled rhombohedral BaTiO₃ crystal was twice higher than that of the [111] poled tetragonal BaTiO₃ crystal. This suggests that the effect of the number of the equivalent domains on the piezoelectric properties is significant larger than that of θ . On the other hand, the [001] poled monoclinic BaTiO₃ crystal had 4 equivalent domains and θ of 45.0° while the [111] poled monoclinic BaTiO₃ crystal had 3 equivalent

domains and θ of 35.3° . The comparison of these two piezoelectric constants revealed that d_{33} of the [001] poled monoclinic BaTiO₃ crystal was twice higher than that of the [111] poled monoclinic BaTiO₃ crystal. As the above mentioned, when the number of

the equivalent domains constructing the engineered domain was same, the smaller angle θ caused the larger piezoelectric properties. However, even if considering the difference of θ , this result revealed that the role of the number of the equivalent domains on the piezoelectric properties is the more significant.

The above discussion gave us a new direction to obtain the best engineered domain configuration for the piezoelectric application. The 1st step is to find the engineered domain configuration with the maximum number of the equivalent domains. For the normal perovskite-type ferroelectric single crystals, only the [001] poled monoclinic and rhombohedral crystals can satisfy this request. The 2nd step is to find the engineered domain configurations with the minimum θ . For the normal perovskite-type ferroelectric single crystals, only the [001] poled monoclinic crystals can satisfy the 2nd request. Therefore, the best engineered domain configuration for the piezoelectric application can be found in the [001] poled monoclinic single crystals.

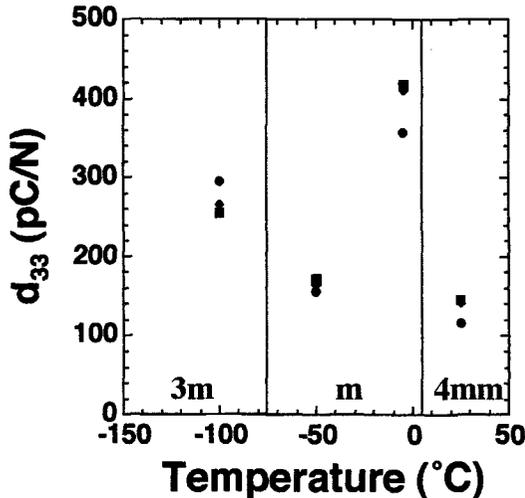


Fig. 12 The d_{33} vs temperature curve of the [001] oriented BaTiO₃ single crystals from -100 °C to 25 °C.

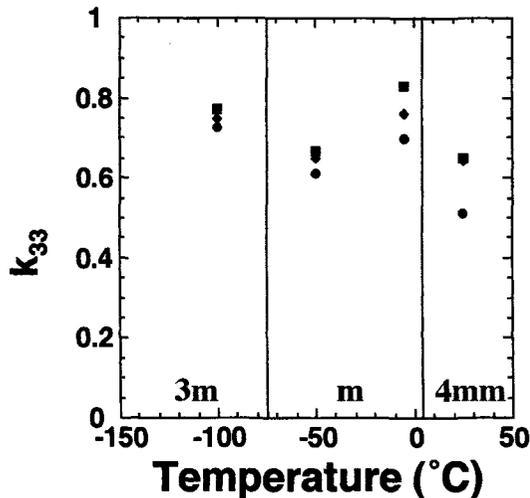


Fig. 13 The k_{33} vs temperature curve of the [001] oriented BaTiO₃ single crystals from -100 °C to 25 °C.

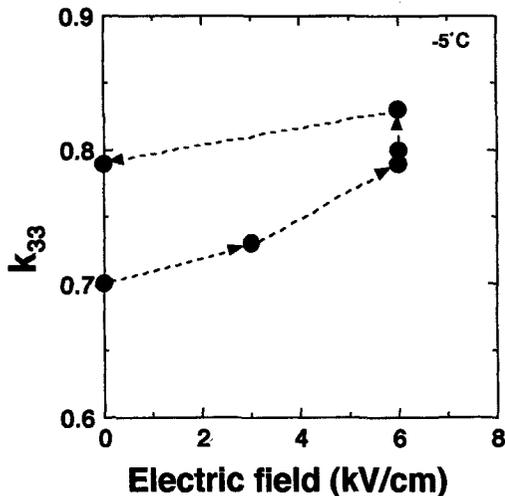


Fig. 14 The k_{33} vs electric-field curve of the [001] poled monoclinic BaTiO₃ single crystals at -5 °C.

3.2 Low electric-field piezoelectric measurements

In the previous section, the higher piezoelectric

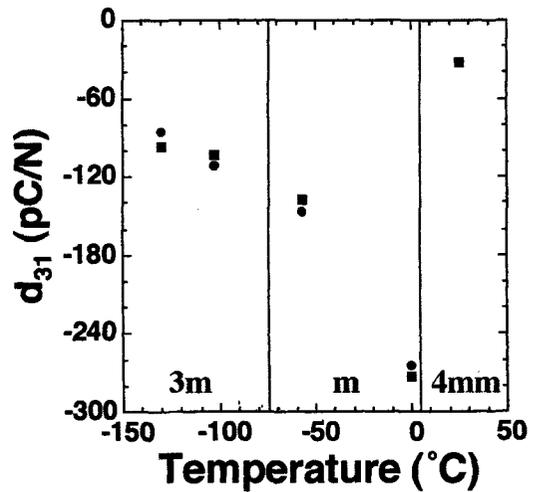


Fig. 15 The d_{31} vs temperature curve of the [001] oriented BaTiO₃ single crystals from -130 °C to 25 °C.

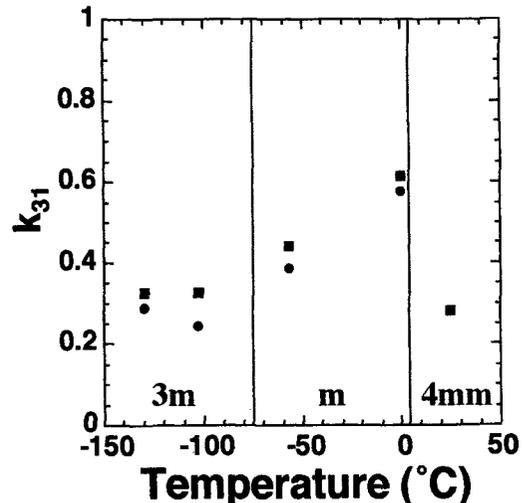


Fig. 16 The k_{31} vs temperature curve of the [001] oriented BaTiO₃ single crystals from -130 °C to 25 °C.

properties in the [001] poled monoclinic and rhombohedral BaTiO₃ crystals was expected. Thus, using the IEEE resonance technique, other piezoelectric properties such as an electromechanical coupling factor and a dielectric constant were investigated for the [001] oriented BaTiO₃ crystals. Figures 12 and 13 show the d_{31} and k_{31} vs temperature curves of the [001] oriented BaTiO₃ crystals. As expected, the [001] poled monoclinic BaTiO₃ crystals exhibited the maximum d_{31} of 415 pC/N and k_{31} of 0.85 at -5 °C, as shown in Fig. 14. These values were much higher than those of PZT ceramics. On the other hand, Figs. 15 and 16 show the d_{31} and k_{31} vs temperature curves of the [001] oriented BaTiO₃ crystals. As expected, the [001] poled monoclinic BaTiO₃ crystals exhibited the maximum d_{31} of -280 pC/N and k_{31} of 0.65 at 0 °C.

The above results indicated that for the BaTiO₃ single crystals, the combination of the monoclinic phase and the [001] crystallographic direction exhibited the best piezoelectric properties. It is well known that the [001] poled tetragonal BaTiO₃ crystals show the d_{31} of 90 pC/N, and k_{31} of 0.56.¹² Therefore, the introduction of the best engineered domain configuration into the BaTiO₃ crystals resulted in the 5 times larger d_{31} and 1.5 times higher k_{31} . Moreover, if the [001] poled monoclinic single crystals were obtained at room temperature, we can expect the much higher piezoelectric properties. Thus, potassium niobate (KNbO₃) may have the higher potential for the piezoelectric applications because of its monoclinic phase at room temperature. However, about the role of the engineered domain configuration, there are still a lot of questions. To clear these unknown things, the much harder study should be required.

4. CONCLUSION

Domain engineering is one of the key techniques to obtain the enhanced piezoelectric and ferroelectric related properties for ferroelectric single crystals. One of the domain engineering techniques is the engineered domain configurations. This domain technique uses the anisotropy of the ferroelectric single crystals as a function of crystallographic orientation. For example, if rhombohedral crystal (polar direction of [111]) is used, the directions for the use of the engineered domain is [100] and [110] directions. Moreover, the crystal structures are also important factor for the engineered domain configurations. To investigate the effect of the crystal structures on the piezoelectric performance, the strain vs temperature behaviors of the [001] and [111] poled BaTiO₃ single crystals were measured from -100 °C to 200 °C. In this temperature region, there were four kinds of the engineered domain configurations with tetragonal, monoclinic and rhombohedral phases. As the results, in the [001] poled monoclinic BaTiO₃ single crystals, the highest piezoelectric performance with d_{31} of 470 pC/N, k_{31} of 0.85, d_{31} of -280 pC/N and k_{31} of 0.65 was obtained, and these values were much higher than those of PZT ceramics. Thus, the relationship between the crystal structures and the crystallographic orientations were discussed. Finally, a new direction to obtain the best engineered domain configuration for the piezoelectric application was proposed. The 1st step

is to find the engineered domain configuration with the maximum number of the equivalent domains constructing the engineered domain configurations. For the normal perovskite-type ferroelectric single crystals, only the [001] poled monoclinic and rhombohedral crystals can satisfy this request. The 2nd step is to find the engineered domain configurations with the minimum angle θ between the polar direction and the electric-field direction. For the normal perovskite-type ferroelectric single crystals, only the [001] poled monoclinic crystals can satisfy the 2nd request. Therefore, the best engineered domain configuration for the piezoelectric application can be found in the [001] poled monoclinic single crystals. If the [001] poled monoclinic single crystals were obtained at room temperature, we can expect the much higher piezoelectric properties. Now, we are trying to find many ferroelectric single crystals with the best piezoelectric performance. The much harder work should be required.

5. ACKNOWLEDGMENTS

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