Transactions of the Materials Research Society of Japan 32[1] 3-6 (2007)

Proposal of New Electromechanical Poling Treatment for Barium Titanate Single Crystals

Satoshi Wada, Tomomitsu Muraishi, Keisuke Yokoh, Hirofumi Kakemoto and Takaaki Tsurumi
Department of Metallurgy and Ceramics Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, JAPAN.
Fax: +81-3-5734-2514, e-mail: swada@ceram.titech.ac.jp

The phase transition behaviors of the [111] oriented barium titanate ($BaTiO_3$) single crystals were investigated as functions of temperature, uniaxial stress and electric fields. For the phase transition by temperature, with decreasing temperature above Tc, the paraelectric phase changed to the intermediate phase with superparaelectric state, and finally change to the ferroelectric phase with randomly oriented spontaneous polarizations. Moreover, it was also found that the phase transition by uniaxial stress field above Tc was almost similar one by temperature. On the other hand, for the phase transition by electric field above Tc, with increasing electric field, the paraelectric phase changed to the intermediate phase, and finally changed to the ferroelectric phase with the oriented polar direction. These results suggested that above Tc, combination between uniaxial stress and electric fields might be effective for a poling treatment of $BaTiO_3$ crystals. Thus, in this study, a new poling method for the $BaTiO_3$ crystals was proposed using control of temperature, uniaxial stress and electric fields.
Key words: barium titanate, engineered domain configuration, electromechanical poling, piezoelectric property

1. INTRODUCTION

Recently, lead-free ferroelectrics became to highly attractive materials on the viewpoint of a solution of the environmental problem[1]. However, as compared with $Pb(Zr,Ti)O_3$ (PZT) ceramics[2], these ferroelectric related properties were very low, and it is difficult to replace the PZT ceramics. Many researchers tried to improve their piezoelectric properties by the chemical modification of lead-free ferroelectrics such as bismuth layer-structure ferroelectrics, barium titanate ($BaTiO_3$) and potassium niobate, but at present, high improvement of the piezoelectric properties was not achieved. On the other hand, there is still a possibility that a new ferroelectric with a new chemical formula can show high piezoelectric performance, but it took over 50 years after finding of $BaTiO_3$. Now, we believe that to achieve the high piezoelectric property similar to that of PZT ceramics, the domain engineering technique should be applied to lead-free ferroelectric materials. The domain engineering is an important technique to obtain the enhanced piezoelectric properties for ferroelectric single crystals. In $[001]_c$ oriented rhombohedral PZN-PT single crystals, (the subscript *c* means the cubic notation system) ultrahigh piezoelectric activities were found by Park et al.[3-4] and Kuwata et al.[5-6] and these ultrahigh piezoelectric properties originated from one of the domain engineering techniques, i.e., "the engineered domain configuration"[7-9]. Recently in the tetragonal $BaTiO_3$ crystals with the engineered domain configurations, it was found that the piezoelectric properties were significantly improved with decreasing domain sizes, and were larger than those of PZT ceramics[9-11]. These results suggested that the domain walls in the engineered domain configuration could contribute significantly to the piezoelectric properties. In general, to induce the engineered domain configuration with the finer domain sizes, higher electric field over 10 kV/cm must be applied to $BaTiO_3$ crystals just above Tc. However, higher electric field exposure above Tc easily leads to a break of crystals. Therefore, to avoid the break of $BaTiO_3$ crystals, electric field for poling treatment must be reduced below 10 kV/cm above Tc. In the above poling treatment, the electric field induced phase transition from cubic to tetragonal is always used. It is well-known that the ferroelectric phase transition is affected by temperature, electric field and stress field. Thus, application of uniaxial stress field to poling treatment in addition of temperature and electric field may reduce a value of electric field below 10 kV/cm above Tc. In this study, for this objective, the phase transition of the $[111]_c$ oriented $BaTiO_3$ crystals was investigated as functions of temperature, uniaxial stress and electric fields. Moreover, on the basis of this results, a new poling method for the $BaTiO_3$ crystals will be proposed using control of temperature, uniaxial stress and electric fields.

2. EXPERIMENTAL

$BaTiO_3$ single crystals were grown by a top seeded solution growth (TSSG) method at Fujikura, Ltd.[12]. These crystals were oriented along [111]c direction using a back-reflection Laue method. For the piezoelectric measurement using the 31 resonators, $BaTiO_3$ single crystals were sized into 4.0x1.2x0.4 mm^3 (4.0mm // $[1\text{-}10]_c$, 1.2mm // $[11\text{-}2]_c$, 0.4mm // $[111]_c$). The domain configuration was observed under crossed-nicols using a polarizing microscope (Nikon, LAB-OPHOTO2-POL). After poling, piezoelectric properties were measured by a

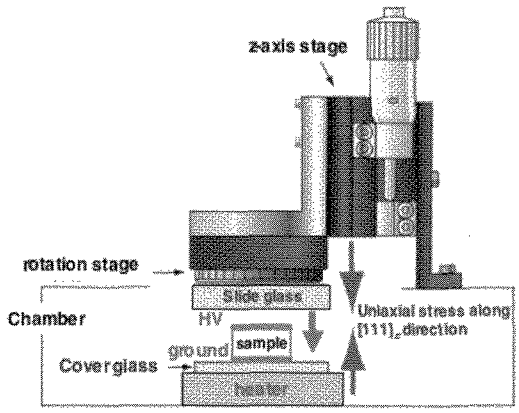

Fig. 1 Schematic new poling attachment controlled by temperature, uniaxial stress field and electric field.

resonance-antiresonance method[13] using impedance analyzer (Agilent, 4294A). In this study, temperature, electric field and uniaxial stress field must be controlled independently. For this purpose, a new poling attachment was designed as shown in Fig. 1. Temperature can be changed from -190 to 600 °C while electric field and uniaxial stress field are applied along the $[111]_c$ directions independently. However, in this study, a uniaxial stress field was applied using a z-axis stage, and a precise uniaxial pressure value was not measured. Thus, a moving length of the z-axis stage from a position of z-axis stage at contact with sample without pressure was defined as apparent uniaxial stress field through this manuscript

3. RESULT AND DISCUSSION

First, the phase transition behavior of the $BaTiO_3$ crystals only by temperature was investigated without electric field and uniaxial stress field by domain observation under crossed-nicols. It was clearly observed that from temperature above Tc, with decreasing temperature, the paraelectric phase changed to an intermediate phase with superparaelectric state, and finally change to the ferroelectric phase with randomly oriented spontaneous, as shown in Fig. 2. A crystal structure of the intermediate phase with superparaelectric state is still unknown, but under crossed-nicols, crystals was always bright when the crystal was rotated, which suggested that this phase is not paraelectric cubic phase. Next, above Tc, the phase transition behavior of the $BaTiO_3$ crystals only by electric field applied along the $[111]_c$ direction was investigated without uniaxial stress field by domain observation under crossed nicols. As the result, with increasing electric field, the paraelectric phase changed to the intermediate phase with superparaelectric state, and finally changed to the ferroelectric tetragonal phase with three oriented polar directions along $[100]_c$, $[010]_c$ and $[001]_c$, as shown in Fig. 3. It should be noted that at the temperature of (Tc + 1.5) °C, the electric-field over 10 kV/cm is required to induce tetragonal phase. Finally, above Tc, the phase transition behavior of the $BaTiO_3$ crystals only by uniaxial stress field applied along the $[111]_c$ direction was investigated without electric field. As the result, with increasing uniaxial stress field, the paraelectric phase changed to the intermediate phase with superparaelectric state, and finally change to the ferroelectric phase with randomly oriented spontaneous, as shown in Fig. 4. When a poling treatment was performed

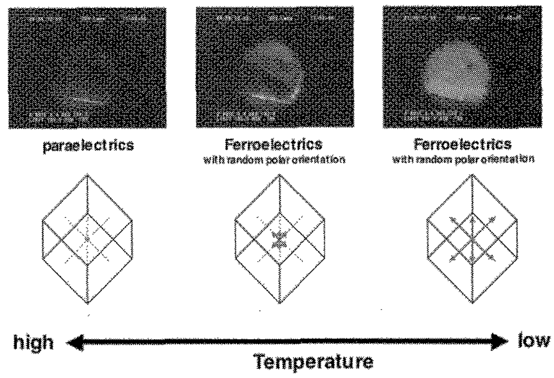

Fig. 2 Phase transition behavior of the $BaTiO_3$ crystals by temperature without electric field and uniaxial stress field.

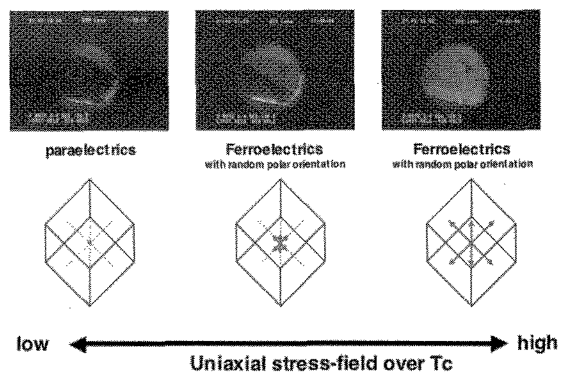

Fig. 3 Phase transition behavior of the $BaTiO_3$ crystals by uniaxial stress field without electric field at (Tc + 1.5) °C.

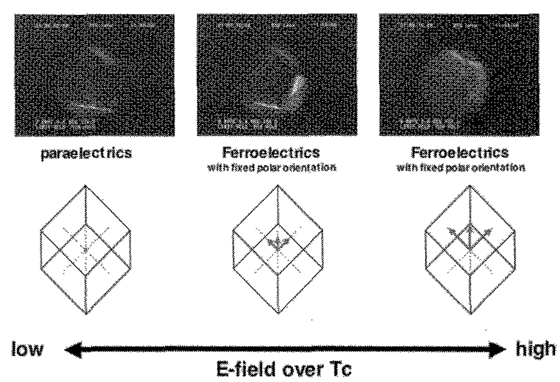

Fig. 4 Phase transition behavior of the $BaTiO_3$ crystals by electric field without uniaxial stress field at (Tc + 1.5) °C.

using electric field, the higher electric field was required with increasing temperature above Tc. On the other hand, when a poling treatment was performed using uniaxial stress field, the smaller uniaxial stress field was enough for fully poled state with increasing temperature above Tc. This is because that the $BaTiO_3$ crystal is ferroelectric and ferroelastic, which suggested that uniaxial stress field is quite effective for a poling treatment of the $BaTiO_3$ crystals.

The above discussion revealed that a phase transition behavior from cubic to tetragonal by temperature and uniaxial stress field was quite similar because of formation of the ferroelectric phase with randomly oriented spontaneous. On the other hand, a phase transition behavior by electric field leads to the ferroelectric tetragonal phase with three oriented polar directions.

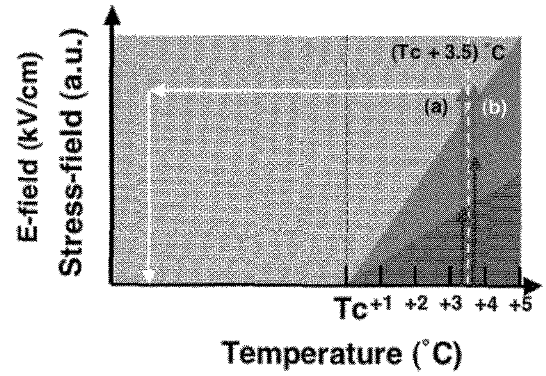

Fig. 5 Two kinds of poling treatments at (Tc + 3.5) °C; (a) lower uniaxial stress field and then higher electric field and (b) higher uniaxial stress field and then lower electric field.

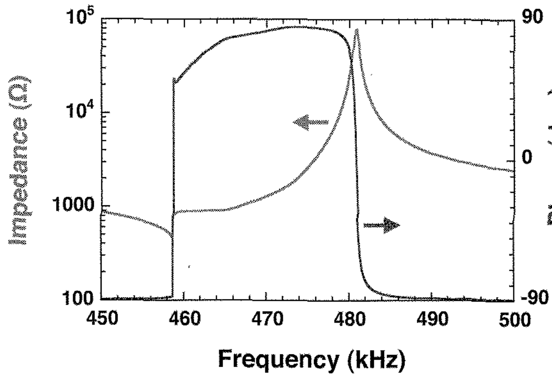

Fig. 6 Frequency dependence of impedance and phase for $[111]_c$ poled $BaTiO_3$ 31 resonator after the poling treatment (a).

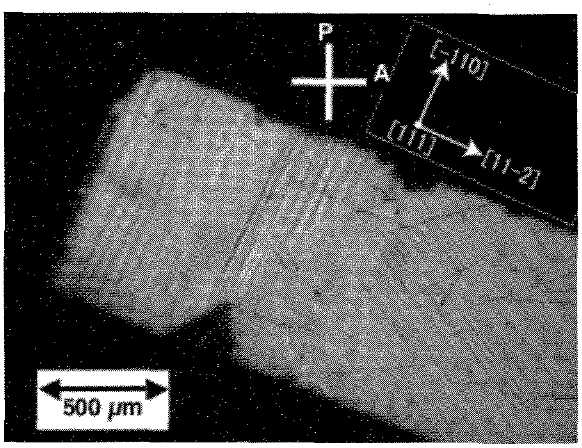

Fig. 7 Domain configuration after the poling treatment (a).

However, it was considered that a phase transition from cubic to the intermediate phase with superparaelectric state by temperature, uniaxial stress field and electric field was completely same behavior. These results suggested that above Tc, the combination between uniaxial stress and electric fields might be effective for the poling of ferroelectric single crystals. Thus, this means that an electric field for a poling treatment above Tc can reduce by a new poling treatment with combination between uniaxial stress field and electric field.

Thus, in this study, a new poling method for the $BaTiO_3$

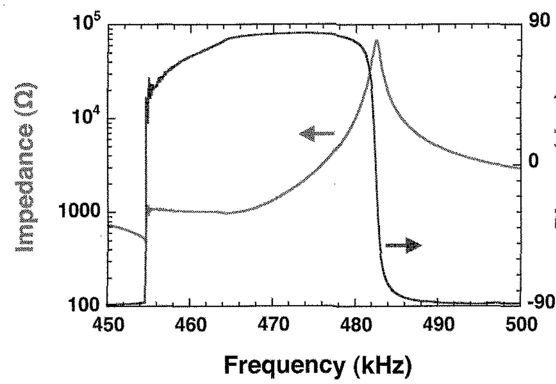

Fig. 8 Frequency dependence of impedance and phase for $[111]_c$ poled $BaTiO_3$ 31 resonator after the poling treatment (b).

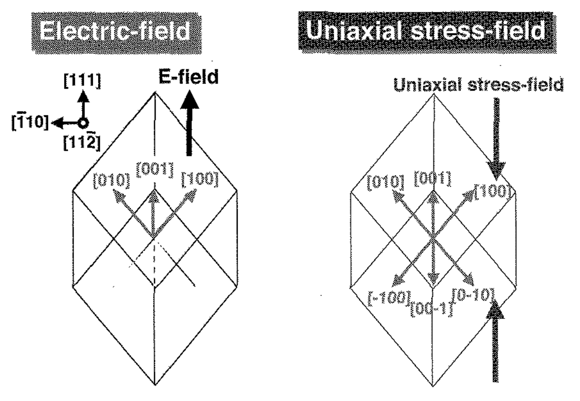

Fig. 9 Effect of electric and uniaxial stress fields for $[111]_c$ oriented $BaTiO_3$ single crystals.

crystals was proposed using control of temperature, uniaxial stress and electric fields. As a poling temperature, (Tc + 3.5) °C was chosen in this study. This is because at this temperature, it is impossible to poll the $BaTiO_3$ crystals using only electric field owing to electric break down. Thus, two kinds of poling treatments at (Tc + 3.5) °C were performed as follows, i.e., (a) lower uniaxial stress field below 10 and then higher electric field above 10 kV/cm and (b) higher uniaxial stress field above 10 and then lower electric field below 10 kV/cm, as shown in Fig. 5. First, a poling treatment (a) was performed, i.e., first, apparent uniaxial stress field of 9 was applied to induce only the intermediate phase with superparaelectric state, and after that, the electric field of 14 kV/cm was applied to induce the ferroelectric phase with the oriented polar direction. As the result, the almost fully poled state was achieved for the $[111]_c$ poled $BaTiO_3$ crystals. Their piezoelectric properties were measured using resonance-antiresonance method as shown in Fig. 6. In Fig. 6, a phase between resonance and antiresonance peaks was almost +90°, which suggested that this poling state was almost fully poled state. Figure 7 shows the domain configuration of the $[111]_c$ poled $BaTiO_3$ crystals. Average domain size in Fig. 7 was over 50 μm, and two kinds of 90° domain configuration was clearly observed. Next, a poling treatment (b) was performed, i.e., first, apparent uniaxial stress field of 17 was applied to induce coexistence between the intermediate and the ferroelectric tetragonal phases, and after that, the electric field of 9.5 kV/cm was applied to induce the ferroelectric phase. As the result, the almost fully poled

TABLE I Piezoelectric related constants for the $[111]_c$ poled $BaTiO_3$ crystals using the poling treatment of (a) and (b).

Poling treatment	ε_{33}^T	s_{11}^E (pN/m²)	d_{31} (pC/N)	k_{31} (%)	d_{33}^* (pC/N)
(a)	2,114	8.7	-136	34	230
(b)	1,983	8.6	-144	37	230

d_{33}^*: measured by d_{33} meter

state was achieved for the $[111]_c$ poled $BaTiO_3$ crystals. Their piezoelectric properties were measured using resonance-antiresonance method as shown in Fig. 8. In Fig. 8, a phase between resonance and antiresonance peaks was almost +90°, which suggested that this poling state was almost fully poled state. The domain configuration by the poling treatment (b) was completely same as Fig. 6. As compared to Figs. 6 and 8, the poling treatment (b) was more effective than the poling treatment (a). Figure 9 shows effects of electric and uniaxial stress fields for the $[111]_c$ oriented $BaTiO_3$ single crystals. In Fig. 9, to prepare fully poled $BaTiO_3$ crystals below Tc, electric field along $[111]_c$ direction can be very effective while uniaxial stress field along $[111]_c$ direction cannot be effective. On the other hand, both electric and uniaxial stress fields were very effective for phase transition from cubic to intermediate phase with superparaelectric state above Tc. Therefore, the intermediate phase with superparaelectric state can become stable in a certain region by control of temperature, electric and uniaxial stress fields, and for the poling treatment (b), the higher uniaxial stress field might be effective to make $BaTiO_3$ crystal the intermediate phase with superparaelectric state near the boarder line between the intermediate and tetragonal states.

On the basis of two impedance curves, piezoelectric related constants for the $[111]_c$ poled $BaTiO_3$ crystals were determined as shown in TABLE I. In TABLE I, the d_{33} was measured using d_{33} meter. It was reported that the d_{33} along the $[111]_c$ direction is calculated as 224 pC/N for $BaTiO_3$ single domain crystal[14]. In this study, the measured d_{33} was 230 pC/N and this value was almost consisted to the calculated value. This revealed that the uniaxial stress field is very effective for the poling treatment above Tc to reduce electric field below 10 kV/cm.

4. CONCLUSIONS

In this study, the phase transition behavior from cubic to tetragonal for the $[111]_c$ oriented $BaTiO_3$ crystals was precisely investigated as functions of temperature, electric field and uniaxial stress field. As the result, it was revealed that above Tc, combination between uniaxial stress field and electric field was very effective for the poling treatment of ferroelectric single crystals. Thus, the new poling method for the $BaTiO_3$ crystals was proposed using a combination of temperature, uniaxial stress field and electric fields, and the almost fully poled state was achieved for the $[111]_c$ poled $BaTiO_3$ crystals.

5. ACKOWLEDGWMENT

We would like to thank Mr. O. Nakao of Fujikura Ltd. for preparing the TSSG-grown $BaTiO_3$ single crystals with excellent chemical quality. This study was partially supported by (1) a Grant-in-Aid for Scientific Research (16656201) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, (2) the Japan Securities Scholarship Foundation, (3) the Toray Science Foundation, (4) the Kurata Memorial Hitachi Science and Technology Foundation, (5) the Electro-Mechanic Technology Advanced Foundation, (6) the Tokuyama Science Foundation and (7) the Yazaki Memorial Foundation for Science and Technology.

6. REFERENCES

[1] M. Demartin Maeder and D. Damjanovic: *Piezoelectric Materials in Devices*, ed. N. Setter (N. Setter, Lausanne, 2002) p.389.
[2] B. Jaffe, W. R. Cook, Jr. and H. Jaffe: *Piezoelectric Ceramics*, (Academic Press, New York, 1971) p.135.
[3] S .-E. Park and T. R. Shrout: *Mater. Res. Innovat.* **1** 20 (1997).
[4] S.-E. Park and T. R. Shrout: *J. Appl. Phys.* **82** 1804 (1997).
[5] J. Kuwata, K. Uchino and S. Nomura: *Ferroelectrics* **37** 579 (1981).
[6] J. Kuwata, K. Uchino and S. Nomura: *Jpn. J. Appl. Phys.* **21** 1298 (1982).
[7] S. Wada, S.-E. Park, L. E. Cross and T. R. Shrout: *J. Korean Phys. Soc.* **32** S1290 (1998).
[8] S. Wada, S.-E. Park, L. E. Cross and T. R. Shrout: *Ferroelectrics* **221** 147 (1999).
[9] S. Wada, H. Kakemoto and T. Tsurumi: *Mater. Trans.* 45 178 (2004).
[10] S. Wada and T. Tsurumi: *Br. Ceram. Trans.* **103** 93 (2004).
[11] S. Wada, K. Yako, H. Kakemoto, J. Erhart and T. Tsurumi: *Key Eng. Mater.* **269** 19 (2004).
[12] S. Ajimura, K. Tomomatsu, O. Nakao, A. Kurosaka, H. Tominaga and O. Fukuda, *J. Opt. Soc. Am.* B 9 1609 (1992).
[13] EMAS-6100: Standard of Electronic Materials Manufacturers Association of Japan (1993).
[14] S. Wada, K. Yako, K. Yokoo, H. Kakemoto and T. Tsurumi, *Ferroelectrics*, (2006) in press.

(Received December 26, 2006;Accepted January 15, 2007)