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# Lattice distortion under an electric field in BaTiO<sub>3</sub> piezoelectric single crystal

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## Abstract

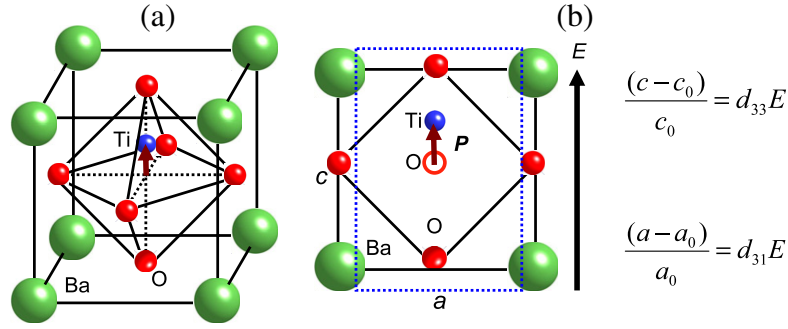
Lattice distortions under an electric field in a mono-domain of BaTiO<sub>3</sub> ferroelectric crystal have been detected with synchrotron x-ray radiation. The variation of the lattice constant with an electric field observed with high angle diffraction shows a linear response nature of the piezoelectric effect. When an electric field is applied along the spontaneous polarization direction, the *c*-axis of the lattice elongates and the *a*-axis of the lattice shrinks at a rate of  $d_{33} = 149 \pm 54 \text{ pm V}^{-1}$  and  $d_{31} = -82 \pm 61 \text{ pm V}^{-1}$ ; these represent the longitudinal and transverse piezoelectric coefficients of BaTiO<sub>3</sub> crystal, respectively. These results give an insight into the intrinsic piezoelectric response on the lattice scale in BaTiO<sub>3</sub> that has been widely used to explore high performance lead-free piezoelectric alloys.

(Some figures in this article are in colour only in the electronic version)

Piezoelectricity, which was discovered by Jacques and Pierre Curie in 1880 [1], is the ability of single crystal with noncentrosymmetry (with the exception of point group 432) to develop an electric charge proportional to a mechanical stress or to produce a deformation proportional to an electric field. Such characteristic properties lead naturally to possibilities for sensing and actuating elastic changes and, therefore, are enormously useful [2–4]. Today, piezoelectric ceramics are widely used to produce essential elements for medical ultrasound tomography, inkjet printer heads, and automobile fuel injectors. BaTiO<sub>3</sub> was the first piezoelectric ceramic developed for technical applications [2] in phonograph pickups marketed by Sonotone Cooperation about 1947, and it remains suitable for the exploration of new piezoelectric alloys [5, 6]. Because of its high piezoelectric activity [2, 3], BaTiO<sub>3</sub> is very promising for the realization of lead-free piezoelectrics [7–9] to replace the currently used lead zirconate titanate (PZT).

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In normal ceramics, the random orientation of the individual crystallites imparts an infinite degree of rotational symmetry, which prevents the occurrence of polarity and piezoelectricity within ceramic texture in spite of the inherent polarity of its crystal. However, in ferroelectric materials, such as BaTiO<sub>3</sub>, such polarity can be produced within ceramic texture by electrically poling the ferroelectric domains, in which electric spontaneous polarizations align toward the same direction, in the direction of the applied electric field. The structural complexity of the ceramics and the variety of phenomena that might be involved make it rather difficult to achieve a clear understanding of their piezoelectric properties. In contrast to polycrystalline piezoelectric ceramics, single crystal is an obvious starting point for understanding the piezoelectricity in ferroelectrics. Although BaTiO<sub>3</sub> single crystals have been available for a long time [10, 11] and their piezoelectric properties have been investigated for more than 50 years [10, 12–16], they are not yet fundamentally understood, as is evident from the summary given in table 1. The reported  $d_{33}$  value falls into a range of 68.5–316.6 pm V<sup>-1</sup>,



**Figure 1.** (a) Tetragonal perovskite structure of BaTiO<sub>3</sub>. (b) Piezoelectric effects in a BaTiO<sub>3</sub> lattice with a tetragonal structure. Under the application of an electric field, the Ti displacement is shifted along the electric field direction, giving rise to the lattice distortion (indicated by the dashed lines) of *a*- and *c*-axes with the given relationships, where *a*<sub>0</sub>(*c*<sub>0</sub>) and *a*(*c*) represent the lattice constants for *E* = 0 and ≠ 0, respectively. When an electric field is applied along the direction of spontaneous polarization, the *c*-axis of the lattice elongates, giving rise to a positive value of *d*<sub>33</sub>; in contrast, the *a*-axis of the lattice shrinks, leading to a negative value of *d*<sub>31</sub>.

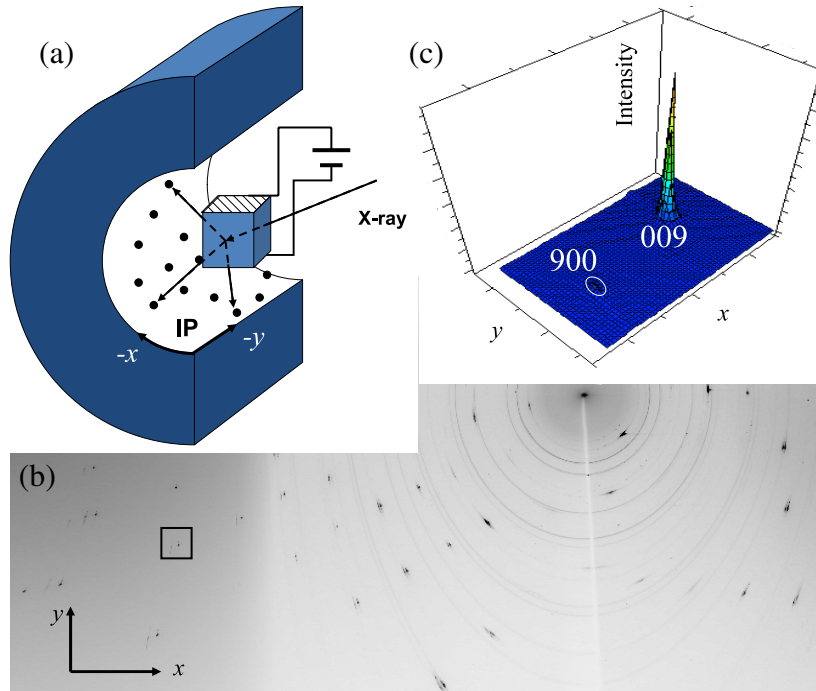
**Table 1.** Piezoelectric coefficients evaluated using synchrotron x-ray radiation at room temperature in the present work in comparison with those reported in the literature and their statistical mean.

	<i>P</i> +	<i>P</i> −	Average				
<i>d</i> <sub>33</sub> (pm V <sup>−1</sup> )	129 ± 60	169 ± 47	149 ± 54				
<i>d</i> <sub>31</sub> (pm V <sup>−1</sup> )	−74 ± 68	−90 ± 54	−82 ± 61				
	Reference [14]	Reference [13]	Reference [15]	Reference [16]	Reference [10]	Reference [12]	Mean
<i>d</i> <sub>33</sub> (pm V <sup>−1</sup> )	68.5	85	90.5	128	132	316.6	136 ± 92
<i>d</i> <sub>31</sub> (pm V <sup>−1</sup> )	−33.4	−34.5	−34.4	—	−57.7	−103.3	−53 ± 30

in which the largest difference is nearly five times. Such a large discrepancy can be attributed to the imperfect poling process in BaTiO<sub>3</sub> single crystal. As shown in figure 1, the piezoelectric effects in tetragonal BaTiO<sub>3</sub> are the effects of coupling between the external electric field and the electric spontaneous polarization (*P*) that arises from the Ti off-centering displacement along the *c*-axis of the tetragonal structure [17–20]. Since there are six equivalent directions for the appearance of spontaneous polarization from the cubic phase at temperature  $T > T_c \approx 120^\circ\text{C}$  [4], 90° and 180° domains are present even in the single crystal. To measure the piezoelectric coefficients with a macroscopic method, such as the mechanical resonance–antiresonance technique [12–14] or the interferometer method [15], a poling process is then required to align all polarizations into the same state. However, as will be shown in our paper, switching all 90° and 180° domains into a mono-domain in single crystal is experimentally difficult. Eventually, the piezoelectric coefficients evaluated by the reported macroscopic methods may not be attributed to the pure responses from a mono-domain in the crystal due to imperfect poling. Here, we report the piezoelectric response in a mono-domain of BaTiO<sub>3</sub> single crystal by directly measuring the lattice distortion of the mono-domain under the application of an electric field using high energy synchrotron x-ray radiation. Such results allowed us to gain an understanding of intrinsic piezoelectric effects in prototypical ferroelectric BaTiO<sub>3</sub> on the lattice scale.

Our experiments were performed using the beam line of BL-1A at the Photon Factory of the high energy accelerator research organization (KEK) in Japan, which has energy

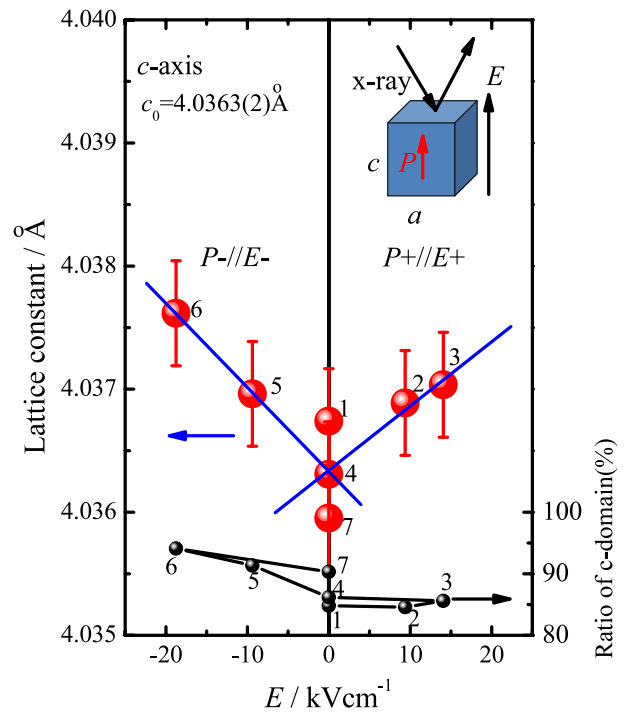
of 18.0 keV and wavelength of 0.6889 Å. Such high energy synchrotron radiation allows us to observe high angle diffraction from single crystal with very strong diffraction intensity, making it possible to reliably determine slight variation in lattice distortion under the application of an electric field. Figure 2 shows the experimental setup for the measurements. A beam line with a diameter of about 1 mm was incident to the *c*-face (for *d*<sub>33</sub> measurements) or the *a*-face (for *d*<sub>31</sub> measurements) of BaTiO<sub>3</sub> single crystal, and the diffractions from the crystal were collected using an imaging plate of a Weissenberg camera installed on beam line BL-1A. Ten minutes were required to obtain a high quality image to collect the x-ray diffraction for each image. A typical image of diffraction patterns from the single crystal is shown in figure 2(b), from which the possible highest angle diffraction of the *c*-face (or *a*-face) was selected to evaluate the lattice constant. The single crystal used in the study was prepared by the Remeika method [11] and has the natural {100} face of the cubic phase. The dielectric measurements show that the crystals used have phase transitions at  $T_c = 401\text{ K}$ , 285 K, 200 K for heating ( $T_c = 394\text{ K}$ , 279 K, 182 K for cooling), respectively. The transition temperature of the paraelectric–ferroelectric phase is very close to the value of 403 K reported for a crystal pulled from Ti-rich melt [4]. The lattice constants obtained at zero field for the *c*-axis ( $c_0 = 4.0363\text{ Å}$ ) and *a*-axis ( $a_0 = 3.9958\text{ Å}$ ; see also figures 3 and 4) are also in good agreement with the acceptable values ( $c_0 = 4.0361\text{ Å}$ ,  $a_0 = 3.9920\text{ Å}$ ) [4] for BaTiO<sub>3</sub> at room temperature. A surface layer of about 20 μm was removed using phosphoric acid at 160 °C before the single crystal was cut into a sample with



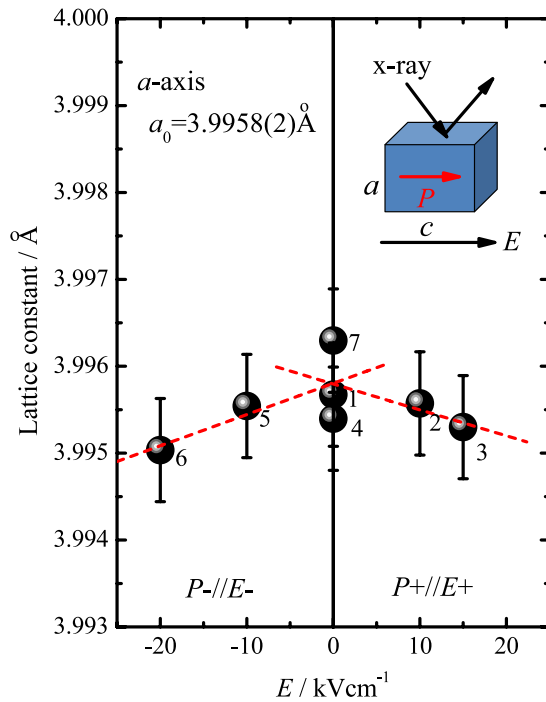
**Figure 2.** (a) Experimental arrangements used in the synchrotron radiation measurements under the application of an electrical field. (b) Typical diffraction pattern for the BaTiO<sub>3</sub> crystal used obtained from the imaging plate (IP). (c) Three-dimensional image of the 900 and 009 reflections from the mono-domains of BaTiO<sub>3</sub> single crystal (the square area indicated in (b)). As is indicated by the circle in (c), the 900 reflection is very weak in comparison with the 009 reflection.

length = 500  $\mu\text{m}$ , width = 300  $\mu\text{m}$ , and thickness = 320  $\mu\text{m}$  (the thickness direction is normal to the {100}-face). Both sides of the {100}-face were coated with a 100 nm thick Au electrode for the application of an electric field in the direction of spontaneous polarization. A Keithley Model 248 high voltage supply was used to provide the voltage source.

Figure 3 shows the results for a *c*-axis lattice distortion with an electric field. In this measurement, the electric field was applied in the direction of the spontaneous polarization along the *c*-axis direction. This configuration allowed us to directly measure the longitudinal piezoelectric effect of the BaTiO<sub>3</sub> tetragonal lattice. The diffraction patterns indicate that the single crystal is not in a mono-domain state but consists of a *c*-axis mono-domain and an *a*-axis mono-domain, as shown in figure 2(c). In the initial state, the *c*-axis mono-domain has a volume fraction of 84% of the crystal (see also figure 3). The 009 reflection was used to measure the variation of the lattice constant with the electric field. The measurement was first performed for the positive (*E*+) direction and then changed to the negative direction. It must be noted that the applied electric field is at least ten times larger than the coercive field ( $\approx 1 \text{ kV cm}^{-1}$ ) of BaTiO<sub>3</sub> single crystal [21]. Thus, the switchable domains are switched, and the lattices elongate under the application of the electric field if a piezoelectric effect is active. As expected, both the positive and negative electric field measurements clearly show the linear expansion of the *c*-axis of the lattice, indicating that the lattice distortion in BaTiO<sub>3</sub> with the applied field has a piezoelectric nature. From the linear relationship of the lattice constant and the electric field, the longitudinal piezoelectric coefficient  $d_{33}$  was estimated to be  $129 \pm 60 \text{ pm V}^{-1}$  and  $169 \pm 47 \text{ pm V}^{-1}$



**Figure 3.** Left axis: lattice constant *c* versus electric field *E*, which was applied along the direction of the electric spontaneous polarization (*P*). The configuration of the crystal is shown in the inset. The normal of the diffraction face is parallel to the direction of the electric field. Note that the applied electric field is significantly higher than the coercive field ( $\approx 1 \text{ kV cm}^{-1}$ ) [21] of BaTiO<sub>3</sub> single crystal so that the spontaneous polarization can be aligned in the field direction during the measurements. The right axis shows the change of the volume fraction of the *c*-domain. The measurement sequences are also numbered.



**Figure 4.** Lattice constant  $a$  versus electric field  $E$ . The configuration of the crystal is shown in the inset. The normal of the diffraction face is perpendicular to the direction of the electric field. The measurement sequences are also numbered.

for the positive and negative fields, respectively, giving an average of  $149 \pm 54 \text{ pm V}^{-1}$ . It is noteworthy that the large error observed in the measurements is essentially derived from the limited resolution of the IP image. The difference between positive and negative field measurements is probably due to such measurement errors. As summarized in table 1, our results are intermediate between the reported minimum ( $68.5 \text{ pm V}^{-1}$ ) and the maximum ( $316.6 \text{ pm V}^{-1}$ ), and are close to the statistical mean ( $=136 \pm 92 \text{ pm V}^{-1}$ ) of these values reported for BaTiO<sub>3</sub> single crystal.

In addition to the variation of the lattice constant, we also observed the change of the  $c$ -domain volume fraction defined by  $I_{009}/(I_{009} + I_{900})$ , where  $I_{009}$  and  $I_{900}$  represent the intensity of the 009 reflection of the  $c$ -domain and the 900 reflection of the  $a$ -domain, respectively. As shown on the right axis of figure 3, the volume of the  $c$ -domain shows a slight increase from the initial value of 84% to a value of 86% for the positive electric field of  $15 \text{ kV cm}^{-1}$ . It remained nearly unchanged when the electric field was removed. When the electric field was applied to a negative value of  $-20 \text{ kV cm}^{-1}$ , the volume increased significantly. However, its stable value of 90% when the negative field was removed clearly indicates that it is still difficult to reach a perfect poling process with an electric field at  $20 \text{ kV cm}^{-1}$ , which is about twenty times greater than the coercive field for single crystal.

We further investigated the transverse piezoelectric effect in BaTiO<sub>3</sub>. To directly observe the effect, the sample configuration was changed to ensure that the normal of the observed diffraction face is perpendicular to the direction of the electric field, as shown in the figure 4 inset. Like the  $c$ -axis of

the lattice, the  $a$ -axis of the lattice also shows a linear response under the application of an electric field. However, there is a difference between the  $c$ - and  $a$ -axis responses: the  $c$ -axis of the lattice expands under the application of the electric field, leading to a positive piezoelectric coefficient; in contrast, the  $a$ -axis of the lattice shrinks, resulting in a negative piezoelectric coefficient, as expected for the piezoelectric effects in BaTiO<sub>3</sub>, as shown in figure 1(b). The estimated values of  $d_{31}$  for the positive and negative fields are  $-74 \pm 68 \text{ pm V}^{-1}$  and  $-90 \pm 54 \text{ pm V}^{-1}$ , respectively, giving an average of  $-82 \pm 61 \text{ pm V}^{-1}$ . This value is comparable to the statistical mean ( $-53 \pm 30 \text{ pm V}^{-1}$ ) of the reported values shown in table 1, indicating that the observed value is reasonable.

In summary, we investigated the longitudinal and transverse piezoelectric effects in the lattice of a BaTiO<sub>3</sub> monodomain. The values of  $d_{33}$  and  $d_{31}$  were estimated to be  $149 \pm 54 \text{ pm V}^{-1}$  and  $-82 \pm 61 \text{ pm V}^{-1}$ , respectively. These results provide an insight into the intrinsic piezoelectric effects in BaTiO<sub>3</sub> single crystal on the lattice scale.

## Acknowledgments

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