

Capturing instantaneous lattice distortion of tetragonal BaTiO₃ induced by application of voltage for millionths of a second

Piezoelectric crystals macroscopically expand, contract, and deform when an electric field is applied. Inversely, electric polarization is generated in crystals when external stress is applied. Piezoelectric devices utilizing this phenomenon are indispensable to our everyday lives; for example, they are used to control the ejection of ink in ink-jet printers and in the touch panels of cell phones. Nowadays, piezoelectricity is also the key for realizing vibration power generation systems for the so-called energy harvesting technique.

Several mechanisms underlying changes in the size and shape of piezoelectric materials have been discussed. To understand the essence of macroscopic piezoelectric deformation, it is necessary to examine the microscopic origin of piezoelectricity; i.e., how much and how fast atoms are displaced in piezoelectric crystals upon the application of an electric field. The atomic displacement induced by the electric field is too small to be detected; even the movement of a crystal lattice has not yet been fully clarified thus far. In this study, by combining two advanced measurement techniques used at SPring-8, i.e., a single-crystal diffraction technique using high-energy X-rays [1] and a high-speed time-resolved measurement [2,3], we succeeded in the *in situ* observation of the change in the crystal-lattice size of piezoelectric single crystals with a time of microsecond order during piezoelectric vibration.

Figure 1 shows the pump-probe-type time-resolved measurement system for collecting single-crystal diffraction images installed at beamline BL02B1. The synchrotron radiation (SR) is chopped

using an X-ray chopper so that it is synchronized with the waveform of the external voltage. The time resolution of this experiment was 4 μ s. There is a timing adjuster between the X-ray chopper and a voltage pattern generator. Time-resolved single-crystal diffraction spots of ferroelectric piezoelectric BaTiO₃ were measured at 300 K in the ferroelectric tetragonal phase using a single crystal plate of 5 \times 2.5 \times 0.1 mm³ with a pair of gold electrodes. A high-energy SR with a wavelength of $\lambda = 0.35639(2)$ \AA ($E = 35$ keV) was used. This high-energy SR enables us to obtain many diffraction spots from the inner area of the sample owing to the high transmission to the sample. The tetragonal lattice parameters a and c were analyzed precisely by the least-squares method using about 600 diffraction spot positions observed at each time.

Figure 2 shows the time evolution of the tetragonality c/a of BaTiO₃ when an electric voltage of square shape with 600 Hz is applied to the c -axis direction of a BaTiO₃ single crystal. The ferroelectric domain structure and crystal structure of BaTiO₃ expected in each time region are also shown in the bottom panel of Fig. 2. Tetragonal BaTiO₃ has a spontaneous polarization P_s along the c -axis. When the applied voltage is changed from negative (I) to positive, polarization reversal occurs (II), and the crystal lattice in the area of negative polarization slightly contracts in the c -axis direction. At the beginning of the polarization reversal, the lattice parameter in the negative polarization area is mainly observed because the volume ratio of the polarization area is larger than that of the positive area. When

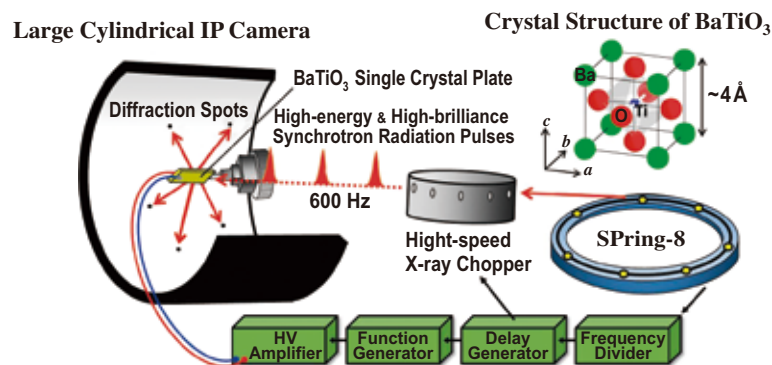


Fig. 1. Time-resolved measurement system for collecting diffraction images installed at BL02B1. The synchrotron radiation is chopped using an X-ray chopper so that it is synchronized with the waveform of the external voltage. There is a timing adjuster between the X-ray chopper and a voltage pattern generator.

the polarization reversal is completed and the whole crystal becomes a positive polarization area (III), the crystal can significantly expand in the c -axis direction. After that, c/a oscillates with decreasing amplitude (IV, V) and finally returns to its original value (VI). This behavior of c/a is similar to the damped oscillation of a spring. The oscillation of c/a observed in the regions III-VI is caused by the piezoelectric vibration of the BaTiO₃ single-crystal plate sample.

Thus, we succeeded in capturing the instantaneous

lattice distortion induced by the application of the voltage for millionths of a second. The achievements of this study are expected to lead to developments in research on the dynamics of atomic displacement of nanosecond or picosecond order and to enable the observation of atoms in an electronic device during operation. Also, this technology is considered to be applicable to the development of new materials for electric storage devices, such as capacitors and batteries.

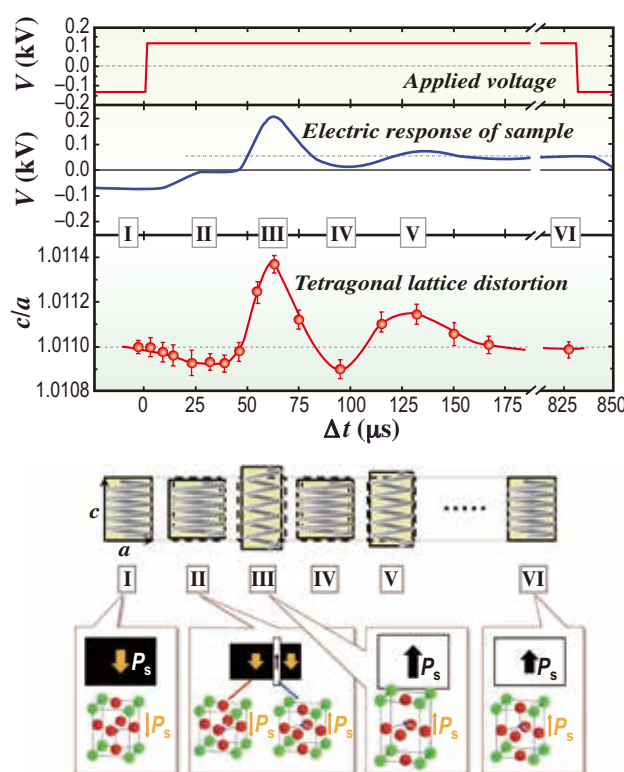


Fig. 2. Change in the tetragonality c/a with respect to time when a cyclic electric voltage of the bipolar square-wave type is applied to the c -axis direction of a BaTiO₃ single crystal. When the applied voltage is changed from negative (I) to positive, polarization reversal occurs (II), and the crystal slightly contracts in the c -axis direction. When the polarization reversal is complete (III), the crystal can significantly expand in the c -axis direction. c/a oscillates with decreasing amplitude and finally returns to its original value (III-VI). This behavior is similar to the damped oscillation of a spring. The ferroelectric domain structure and crystal structure expected in each time region are schematically drawn at the bottom.

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