HIGH-RESOLUTION POWDER DIFFRACTOMETRY OF *h*-$BaTiO_3$

A hexagonal-$BaTiO_3$ is a poly-type structure of $BaTiO_3$ in which the local environment of the Ti atom is very similar to that of the familiar cubic-$BaTiO_3$. Upon cooling to 222 K and 74 K, this structure undergoes successive phase transitions from the prototype hexagonal phase (Phase I) to Phases II and III, respectively [1]. Very little is known about the symmetry and structure of these low temperature phases. X-ray analysis with a single domain crystal and convergent beam electron diffraction have revealed that the space group of the Phase II crystal is $C222_1$ [2,3]. Phase III, a ferroelectric phase, is not as well characterized; some evidence suggests that the crystal symmetry is too low for an orthorhombic space group, and the crystal lattice has been described as either orthorhombic or monoclinic [4,5]. The purpose of the present study is to clarify the symmetry and lattice form of the low temperature phases, especially the ferroelectric phase, in order to understand the mechanism of the phase transition.

High-resolution powder diffraction experiments were performed at beamline **BL02B1** at an energy of 14.329 keV, using a double-flat Si 111 monochromator and Si 220 analyzer [6]. Flat mirrors were used to obtain a parallel beam. Typical ring current during the data accumulation was about 18 mA, since the experiments were performed when SPring-8 was still in its early stages of operation. Samples to be analyzed were placed in a refrigerator-type cryostat which controlled the sample temperature within 0.1K [7,8].

We observed several Bragg reflections as a function of temperature (Fig. 1). High resolution imaging allowed splitting of reflections in Phase III to be clearly seen. Since we used very tight collimation to obtain high resolution, however, the intensity was very weak. In Fig. 2, the width (FWHM) of profiles taken in Phase I is plotted as a function of the diffraction angle. The smallest width obtained was 0.0085°. This value might be the record for powder diffraction obtained at beamline BL02B1 and this high resolution is crucial for our present work. When using a conventional soller-slit system, the intensity increases by two orders of magnitude [6] but the resolution drops to 0.04°.

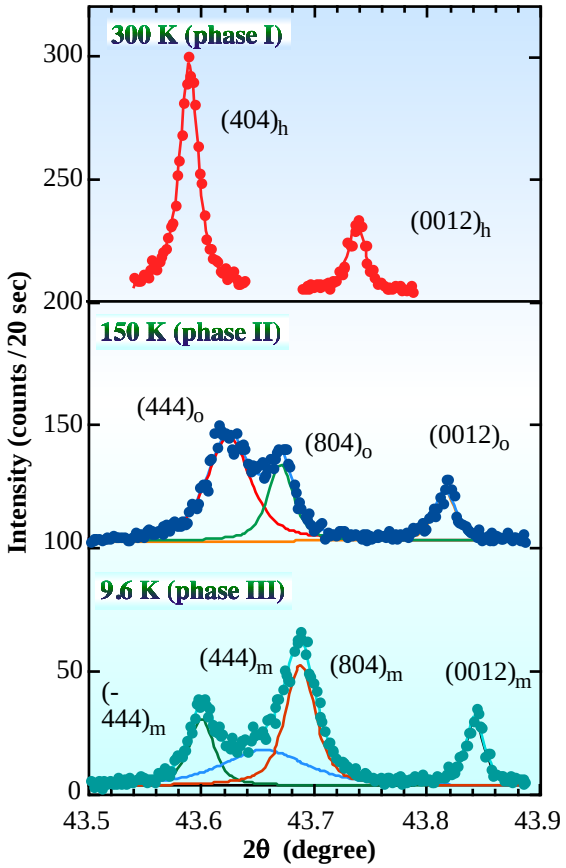

Fig. 1. Change of profiles as a function of temperature [8].

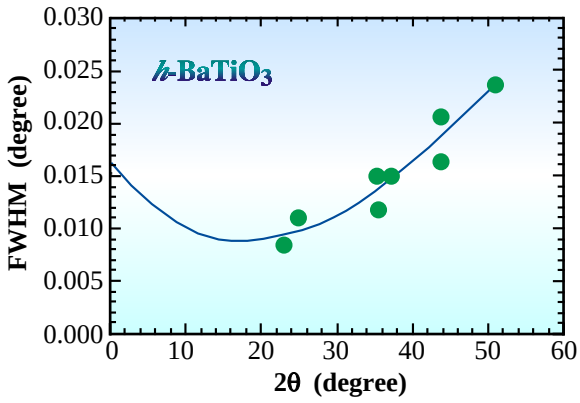

Fig. 2. Observed FWHM of the profiles as a function of diffraction angle [8]. Solid line is calculated one with $(w_0+w_1 tanq+w_2(tanq)^2)^{1/2}$.

The lattice parameters obtained by this high-resolution powder diffraction are depicted in Fig. 3 by closed circles. In the figure, the data are referred to an intermediate orthorhombic cell. We determined that the lattice in Phase III is monoclinic, and the deviation of the γ angle is only 0.08° from 90° in the orthorhombic cell or 0.05° from 120° of the hexagonal cell. In the figure, the lattice parameters later obtained by a high-resolution single crystal experiment at a laboratory system are indicated by open circles, while those obtained by high-resolution neutron scattering are given by cross marks [7-9]. Note that a resolution of powder diffraction at a laboratory system is beyond this type experiment. Further, we would like to emphasize that the single crystal experiments cannot determine the unit cell uniquely because the complicated domain structure takes places associated with the structural phase transition. The space group of Phase II is naturally found to be $C222_1$, which is consistent with previous reports [2,3]. The space group of Phase III is determined to be $C112_1$ if the lattice form is chosen to be an orthorhombic cell with a slight γ angle distortion (Fig. 4). In crystallography, the C-lattice with the γ angle distortion is conventionally chosen as a primitive cell so that the space group is the equivalent to $P112_1$, whose lattice is similar to the hexagonal cell. In Fig. 4, the relationship between the unit cells is shown.

For consideration of the strain in Phase III, the orthorhombic cell is not convenient. Let us therefore convert the unit cell of Phase II and III to the primitive cell as shown in Fig. 4. The hexagonal cell in Phase I is primitive. The C-base orthorhombic cell can be chosen as a primitive cell with the condition of $a_p = b_p$ with the γ angle distortion; that is, it is a special type of monoclinic cell. If all of lattices are chosen as a primitive cell, it is convenient to see the character of the distortion in Phase III which is shown in Fig. 5 (a) and (b). The characteristic point of Phase III seems to be the deviation of

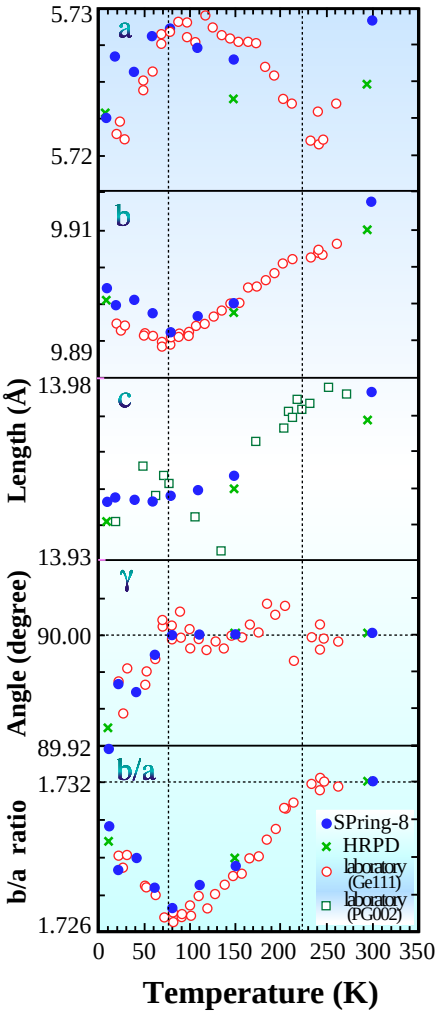

Fig. 3. Lattice parameters referred to the orthorhombic cell as a function of temperature [8].

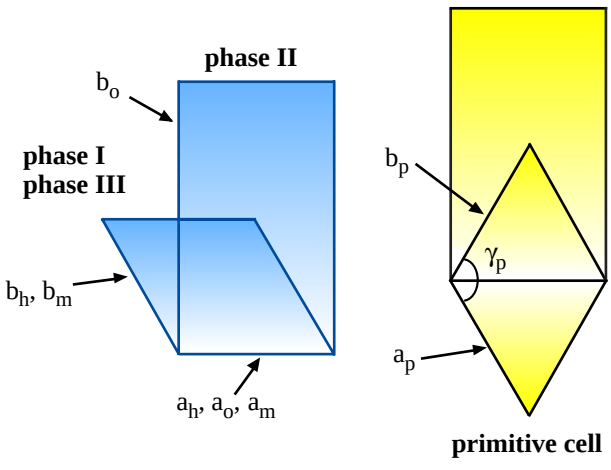

Fig. 4. The relationship of the unit cells of three phases [8].

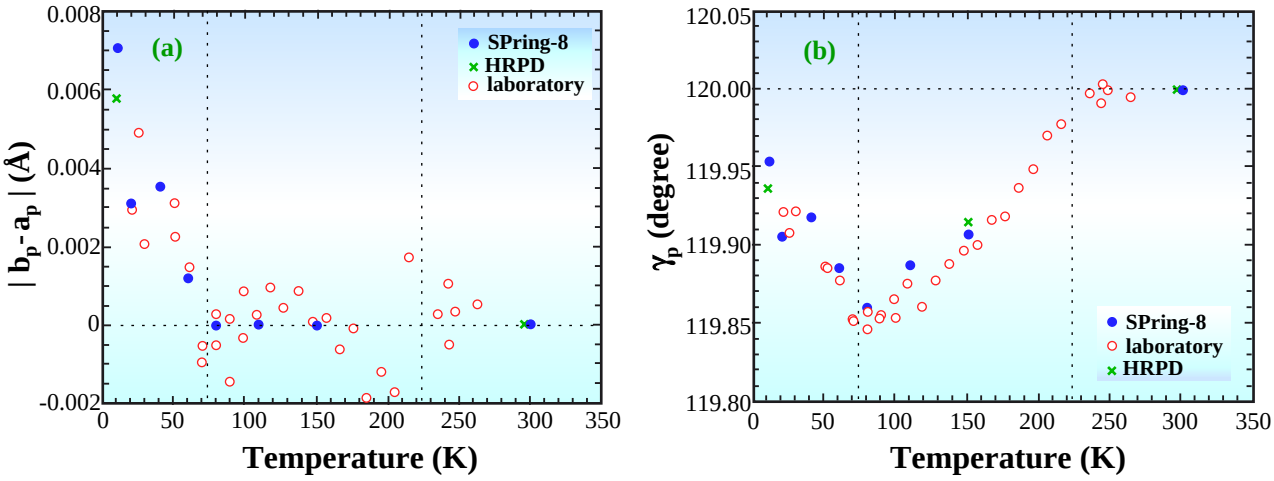

Fig. 5. Observed strain as a function of temperature.

a_p against b_p and the recover of the γ angle distortion. The results indicated that high-resolution experiment was required to distinguish the lattice change of 0.005 Å and the angle distortion of 0.1° and to identify the symmetry of the unit cell of Phase III in *h*-$BaTiO_3$. Detailed structure analyses were successfully performed by a high-resolution neutron experiment [9] based on the symmetry of the unit cells determined in this study.

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References

[1] E. Sawaguchi *et al.*, J. Phys Soc. Jpn. **54** (1985) 480.
[2] T. Yamamoto *et al.*, J. Phys Soc. Jpn. **57** (1988) 3665.
[3] K. Tsuda and M. Tanaka, PhD. Theses, Tohoku University (1991).
[4] E. Sawaguchi *et al.*, Jpn J. Appl. Phys. Suppl. **24** (2) (1985) 252.
[5] E. Sawaguchi *et al.*, Ferroelectrics **106** (1990) 63.
[6] Y. Noda *et al.*, J. Synchrotron Rad. **5** (1998) 485.
[7] Y. Noda *et al.*, Proc. 6th Japan-CIS/Baltic Symposium, Ferroelectrics **217** (1998) 1.
[8] Y. Noda *et al.*, Proc. Int. Conf. SRMS-2, Jpn. J. Appl. Phys. **S38-1** (1999) 73.
[9] Y. Noda, K. Akiyama, T. Shobu, Y. Morii, N. Minakawa and H. Yamaguchi ,Proc. 7th ISSP Int. Symp. (1998); J.Phys. and Chem. Solid **60** (1999) 1415.