MLF Experimental Report	提出日 Date of Report 2011.6.22
課題番号 Project No. 2010A0023 実験課題名 Title of experiment **Investigations of ferroelectric crystal structures for Bi-based perovskite ferroelectric oxides** 実験責任者名 Name of principal investigator Yuji Noguchi 所属 Affiliation RCAST, The Univ. of Tokyo	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/（BL No.） SuperHRPD 実施日 Date of Experiment 2010/ 11/ 27 13/ 00 ~ 2010/ 11/ 29 13/ 00

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Bi-based perovskite ferroelectric oxides

x(Bi,K)TiO3-(1-x)(Bi,Na)TiO3, x=0.00-0.5

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Bismuth sodium titanate [(Bi,Na)TiO_3:BNT][1]-based perovskites have attracted a great deal of attention as a promising candidate for applications in lead-free ferroelectric devices. Although BNT-based ceramics have been intensively studied, a marked enhancement in their properties has not been achieved thus far. The problem with Bi-based ferroelectrics is that Bi vaporization generates defects during fabricating Bi-based devices due to the high vapor pressure of Bi. Defects in ferroelectric materials play an important role in their leakage current, ferroelectric and piezoelectric properties. Therefore, a guiding principle of defect control is required to be established for obtaining high-quality Bi-based devices with superior ferroelectric/piezoelectric properties. Investigations on single crystals are expected to be advantageous to elucidate the fundamental properties and to establish the guiding principle for enhancing ferroelectric properties, because microstructure and grain size does not affect the properties for single crystals.

$x$$Bi_{0.5}K_{0.5}TiO_3$- (1-$x$)$Bi_{0.5}Na_{0.5}TiO_3$ [xBKT-(1-x)BNT] has been extensively studied as a promising lead-free material. BKT-BNT has been reported to have a morphotropic phase boundary (MPB) between the rhombohedral (BNT) and tetragonal (BKT) structures at around x = 0.20[2].

The objective of this study is to elucidate the fundamental structural properties of BKT-BNT through the structural analysis based on high-resolution neutron powder diffraction study.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

【Sample preparation】BKT-BNT powders were prepared by a solid-state reaction. Mixed raw materials were sintered at 800–1000 °C in air. High-resolution neutron powder diffraction (NPD) data were collected by SuperHRPD in KEK, and the data obtained were analyzed by the Rietveld method using the program Z-Rietveld.

【Results and discussion】From X-ray diffraction (XRD) analysis, 113_h(h denotes hexagonal) attributed to rhombohedral *R*3*c* structure was observed for $x \leq 0.22$. XRD showed a peak splitting of 200_c(c denotes cubic) originating from tetragonal *P*4*mm* for $x \geq 0.30$. A structural phase boundary is suggested to be present at $x = 0.22-0.30$. NPD analysis reveals that $x = 0.24$-0.28 exhibits an apparent peak of 113_h. In addition, the peak splitting of 200_c was also observed for $x \geq 0.30$ from NPD analysis.

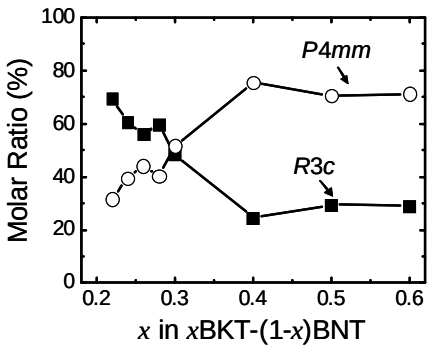

Fig. 1. Molar ratio of *R*3*c* phase and *P*4*mm* phase.

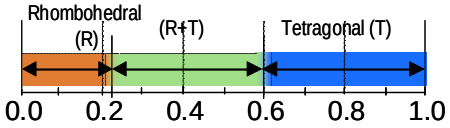

Fig. 2. Phase diagram of BKT-BNT (proposed).

From the results of the Rietveld analysis of NPD data, the followings structural findings were obtained for $x = 0.28$: *R*3*c* single-phase analysis; $R_{wp} = 14.4$ %, *P*4*mm* single-phase analysis; $R_{wp} = 12.6$ %, *R*3*c*-*P*4*mm* 2-phase analysis; $R_{wp} = 11.5$ %（*R*3*c* percentage = 60 mol.%, *P*4*mm* percentage = 40mol.%）. The value of R_{wp} for the *R*3*c*-*P*4*mm* 2-phase analysis was lower by 1−3 % than that for the single phase analysis of *R*3*c* or *P*4*mm*. In the analysis for $0.22 \leq x \leq 0.60$, the *R*3*c*-*P*4*mm* 2-phase analysis yielded a lower R_{wp} than the single-phase analysises. Figure 1 indicates the molar ratio of *R*3*c* phase and *P*4*mm* phase obtained by the Rietveld analsyis. With an increase in *x*, the molar ration of *P*4*mm* phase increased and became constant for $x \geq 0.4$. We propose a phase diagram in the BKT-BNT system shown in Fig. 2.

[1] G. A. Smolenskii *et al*., *Sov. Phys. Solid State*. 2, 2651 (1961). [2] T. Takenaka *et al*., *Jpn. J. Appl. Phys*. 30, 2236 (1991).