MLF Experimental Report	提出日 Date of Report 2011.6.22
課題番号 Project No. 2010B0016 実験課題名 Title of experiment Structural analysis of Pb-free 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 2011/ 3/ 9 13/ 00 ~ 2011/ 3/ 11 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)BiFeO3, x=0.00-0.70

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.

Development of lead-free ferroelectric materials that can replace widely-used lead zirconate titanate (PZT) is becoming increasingly imperative. Ferroelectric $BiFeO_3$ (BFO) with rhombohedral *R*3*c* structure has attracted a great deal of attention because of a very high Curie temperature (T_C) of 830 °C and a large spontaneous polarization (P_s) exceeding 100 μC/cm^2 [1]. BFO-based solid solution ferroelectric materials are expected as materials which can replace PZT. Recently, our group has reported that $x(Bi_{0.5}K_{0.5})TiO_3$(BKT)-(1-*x*)BFO ceramics with $x = 0.40$ exhibit a large remanent polarization (P_r) of 52 μC/cm^2 and a superior piezoelectric property (S_{max}/E_{max} = 190 pm/V) [2].

The objective of this study is to investigate the effects of defect control on the fundamental properties of *x*BKT-(1-*x*)BFO single crystals It is demonstrated that defect control (suppression of the formation of vacancies of Bi and O) at a high oxygen pressure Po_2 is effective for obtaining high-quality and high-performance *x*BKT-(1-*x*)BFO single crystals.

The objective of this study is to elucidate the fundamental structural properties of BKT-BFO 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-BFO 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.

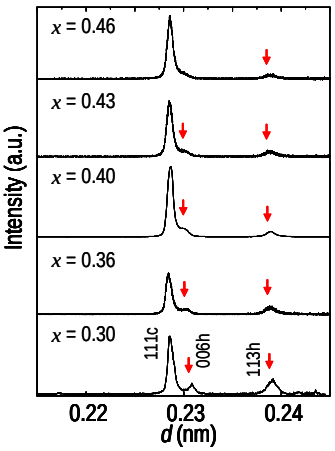

Fig. 1 Neutron powder diffraction data around 111_c for BKT–BFO (x = 0.30–0.46).

【Results and discussion】 Figure 1 shows the NPD patterns around 111_c (c denotes cubic). From the X-ray diffraction (XRD) analysis, 006_h and 113_h(h denotes hexagonal) peaks originating from rhombohedral *R*3*c* structure were observed for $x \leq 0.36$. From the NPD analysis for x = 0.40, 0.43, and 0.46, these peaks attributed to *R*3*c* structure were also detected. These results demonstrate that *R*3*c* phase is present in $0.40 \leq x \leq 0.46$. The Rietveld analysis assuming that two phases composed *R*3*c* and *P*4*mm* structures are present reproduces the NPD data fairly well. Win an increase in x, moral ratio of *R*3*c* phase decreased, e.g., 83 % for x = 0.30 and 66 % for x = 0.46. Figure 2 exhibits the structural parameters obtained by the Rietveld analysis, i.e., tetragonal (*P*4*mm*) distortion expressed by *c*/*a* (parameter c divided by parameter *a*), rhombohedral (*R*3*c*) distortion of α_r (60 ° shows zero distortion). Here, the parameters of BFO (x = 0) and BKT (x = 0) are referred from the Ref. 3 and 4. The samples (x = 0.40) that exhibits superior ferroelectric and piezoelectric properties had the values of $c/a \sim 1.00$、$\alpha_r \sim 59.6$ °. This results show that x = 0.40 is composed of the *R*3*c* phase with an apparent ferroelectric distortion and the *P*4*mm* phase with a very small ferroelectric distortion (hereafter, this phase is referred to as pseudo-cubic phase).

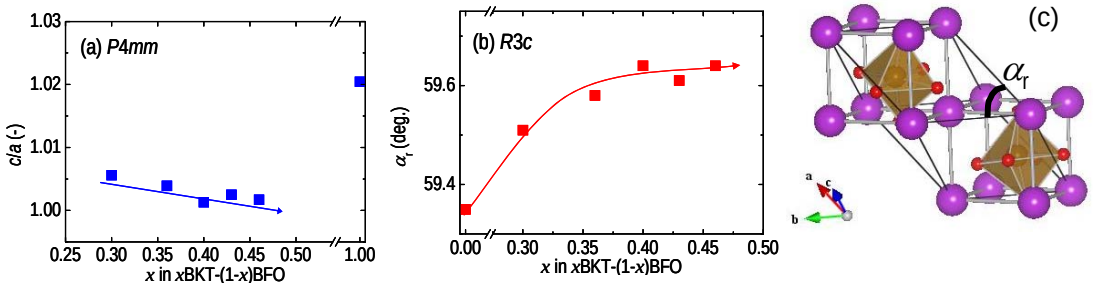

Fig. 2 Structural parameters of (a) tetragonal distortion of *c*/*a* of *P*4*mm* phase and (b) rhombohedral distortion a_r of *R*3*c* phase as a function of composition (x) and (c) crystal structure of *R*3*c* phase.

[1] J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, *Phys. Rev. B*, **2005**, 71, 014113
[2] H. Matsuo, Y Noguchi, M, Miyayama, M, Suzuki, A, Watanabe, S. Sasabe, T. Ozaki, S. Mori, S. Torii, T. Kamiyama, *J. Appl. Phys.*, **2010**, 108, 104103