MLF Experimental Report	提出日 Date of Report 2014/09/11
課題番号 Project No. 2014A0282 実験課題名 Title of experiment Crystal structural analyses of Bi-based perovskite ferroelectrics for establishing their materials design 実験責任者名 Name of principal investigator Yuji Noguchi 所属 Affiliation University of Tokyo	装置責任者 Name of responsible person 石垣 徹 装置名 Name of Instrument/（BL No.） IBARAKI Materials Design Diffractometer (iMATERIA) / (BL-20) 実施日 Date of Experiment 2014.06.09-11

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.

強誘電体粉末

$(1-x)(Bi_{0.5}Na_{0.5})TiO_3-xBaTiO_3$

x = 0, 0.04, 0.06, 0.08, 0.09, 0.10, 0.12

$(1-x)(Bi_{0.5}Na_{0.5})TiO_3-x(Bi_{0.5}K_{0.5})TiO_3$

x = 0.15, 0.20, 0.23, 0.25, 0.27, 0.30, 0.35

$(1-x)(Bi_{0.5}Na_{0.5})TiO_3-xBa(Mg_{1/3}Nb_{2/3})O_3$

x = 0.03, 0.05, 0.07, 0.10

$(1-x)(Bi_{0.5}Na_{0.5})TiO_3-xBa(Zn_{1/3}Nb_{2/3})O_3$

x = 0.03, 0.05, 0.07, 0.10

$(1-x)BiTiO_3-x(Bi_{0.5}Na_{0.5})TiO_3$

x = 0.01, 0.03, 0.05

$(1-x)LiNbO_3-xBiTiO_3$

x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.09, 0.10, 0.15, 0.20

$(1-x)LiNbO_3-xBi(Mn,W)O_3$

x = 0.05, 0.10, 0.20, 0.30

$(1-x)LiNbO_3-xBi(Fe,W)O_3$

x = 0.05, 0.10, 0.20, 0.30

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.

【Introduction】

Ferroelectric $Pb(Zr,Ti)O_3$ has been widely used for piezoelectric devices such as sensors for mobile phones, actuators for fuel injections in cars, and transducers for medical echography. Recently, the studies on

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

lead-free ferroelectric materials have been intensively conducted from environmental and technological points of view. Bismuth sodium titanate [$(Bi,Na)TiO_3$:BNT][1] is considered to be the leading candidate in lead-free materials. Solid solution $(Bi,Na)TiO_3$–$x$$BaTiO_3$ [BNT–xBT] has been reported to show enhanced piezoelectric properties in the form of ceramics with a composition near morphotropic phase boundary (MPB)[2,3]. However, there are some problems to be overcome. One is the problem related to the phase diagram that is still in debate [2-4]: the synthesis of high-purity BNT–BT is quite difficult due to the volatility of Bi [5] giving rise to a deviation of composition and then to a generation of unintentional phase(s).

The objective of this study is to establish a materials design for controlling piezoelectric strain properties in the BNT–BT system. The crystal structures are analyzed by using neutron powder diffraction (NPD) at BL20 in J-PARC.

【Experimental】

High purity $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$x$$BaTiO_3$ (x = 0, 4, 6, 8, 9, 10, 12 %) powders were synthesized by a solid-state reaction adapting a bead-mill processing. Structural characterization was performed by the Rietveld analyses of NPD data collected at BL20 in J-PARC.

【Results】

In the NPD data, superlattice reflections such as $1/2\ \overline{1/2}\ 3/2$ attributed to monoclinic (M) structure in space group *Cc* were detected for $x \leq 4$ %. Superlattice reflections such as $5/2\ 3/2\ 0$ due to tetragonal (T') structure in space group *P*4*bm* with a small *c*/*a* of ~1.00 % were observed for 6 % $\leq x \leq$ 7 %. A splitting of the NPD peaks, e.g., of 200 and 002, due to tetragonal (T) *P*4*mm* structure with a large *c*/*a* of ~1.5 % was observed at $x \geq 8$ %. Figure shows the proposed phase diagram composed of the M(*Cc*), T'(*P*4*bm*), and T(*P*4*mm*) phases with two MPBs in the BNT-BT system obtained by the Rietveld analyses of the NPD data.

[1] G. A. Smolenskii *et al*., *Sov. Phys. Solid State*, **2**, 2651 (1961). [2] T. Takenaka *et al*., *Jpn. J. Appl. Phys*, **30**, 2236-2239 (1991). [3] W. Jo *et al*., *J. Appl. Phys*, **109** (1), 014110 (2011). [4] C. Ma *et al*., *Adv. Funct. Mater*, **23**, 5261-5266 (2013). [5] K. Yamamoto *et al*., *Jpn. J. Appl. Phys*, **47** (9), 7623-7629 (2008).

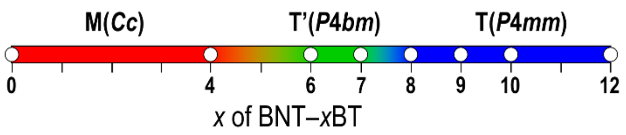

Figure. Phase diagram of the BNT–xBT system obtained by the NPD analysis.