MLF Experimental Report	提出日 Date of Report 2017/2/6
課題番号 Project No. 2016A0132 実験課題名 Title of experiment Reverse Monte Carlo modeling of defect distributions in (Na, Bi)(Ti, M)O_3 (M=Nb and Ta)-based oxide-ion conductors 実験責任者名 Name of principal investigator Yasushi Idemoto 所属 Affiliation Tokyo University of Science	装置責任者 Name of responsible person Toshiya Otomo 装置名 Name of Instrument/（BL No.） NOVA/BL21 実施日 Date of Experiment 2016/6/9 - 2016/6/11 2016/11/26 - 2016/11/27

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.

Compositions: $Na_{0.5}Bi_{0.5-x}TiO_{3-\delta}$, $Na_{0.5+y}Bi_{0.5-y}TiO_{3-\delta}$
Physical form: Powder

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.

Experimental method

$Na_{0.5}Bi_{0.5-x}TiO_{3-\delta}$ and $Na_{0.5+y}Bi_{0.5-y}TiO_{3-\delta}$ with oxide-ion conduction were synthesized by a conventional solid-state reaction method, and then their phases were identified by X-ray diffraction measurements. Metal compositions of the samples were estimated by ICP and atomic absorption analyses.

In order to clarify defect distributions in the crystals, neutron total scattering patterns of the samples were measured by NOVA installed at J-PARC. Each powder with a weight of 0.5~1.0 g was loaded in a vanadium container, and then the scattering pattern was measured at room temperature. The Faber-Ziman structure factors $S(Q)$ were obtained from the lattice constants and the metal compositions, and then reduced pair distribution functions $G(r)$ were calculated by the Fourier transformation of the $S(Q)$. Atomic configurations of the samples were simulated by the Monte Carlo method using the experimental data, which is the so-called reverse Monte Carlo (RMC) technique.

Results

From the average structures refined by the Rietveld analysis using Bragg profiles, simulation boxes for the RMC analysis for $Na_{0.5}Bi_{0.5-x}TiO_{3-\delta}$ and $Na_{0.5+y}Bi_{0.5-y}TiO_{3-\delta}$ were constructed. In the analysis, $S(Q)$ were degraded taking the box sizes into account. In order to obtain accurate atomic configurations, the RMC snapshots were relaxed a couple of times by the density functional theory (DFT) calculation.

Figures 1 and 2 show simulated patterns and an obtained atomic configuration of $Na_{0.5}Bi_{0.45}TiO_{3-\delta}$, respectively. As seen in Fig. 1, the atomic configuration can explain well all the experimental data: that is, the X-ray Bragg profile, the neutron $G(r)$, the neutron and the X-ray $S_{box}(Q)$. From the atomic configuration (Fig. 2), it is indicated that an atomic arrangement around Bi is distorted significantly compared with that around Na. Such a distortion seems to be unfavorable for oxide-ion conduction.

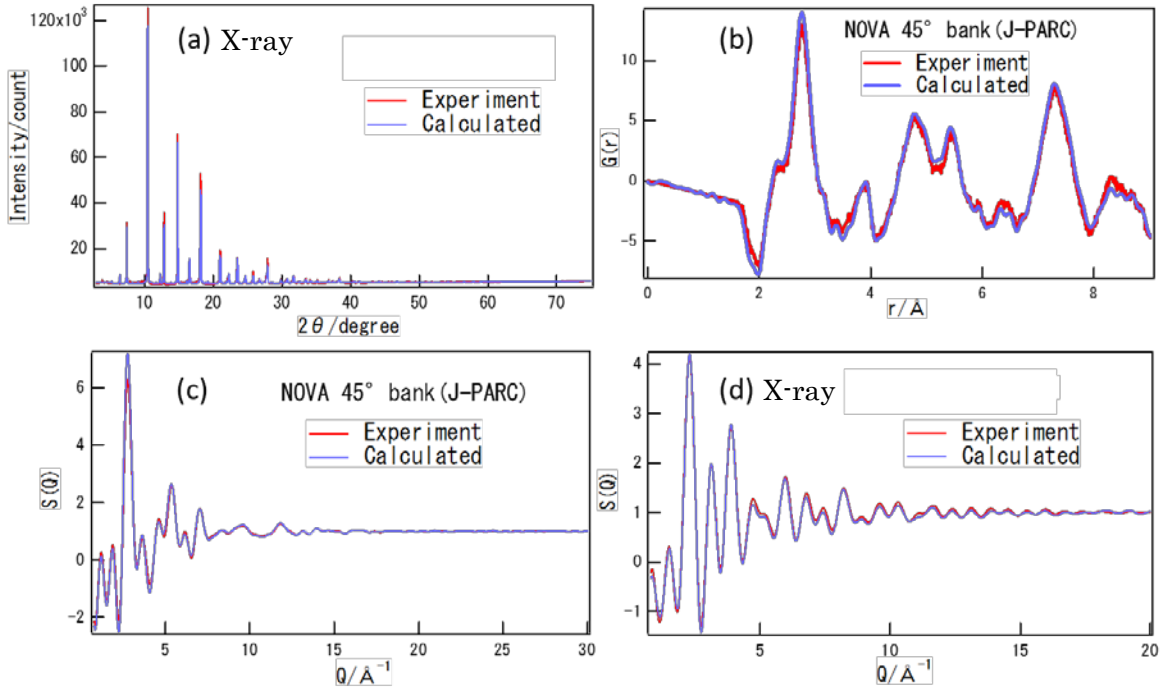

Fig. 1 (a) X-ray Bragg profile, (b) neutron $G(r)$, (c) neutron and (d) X-ray $S_{box}(Q)$ of $Na_{0.5}Bi_{0.45}TiO_{2.925}$.

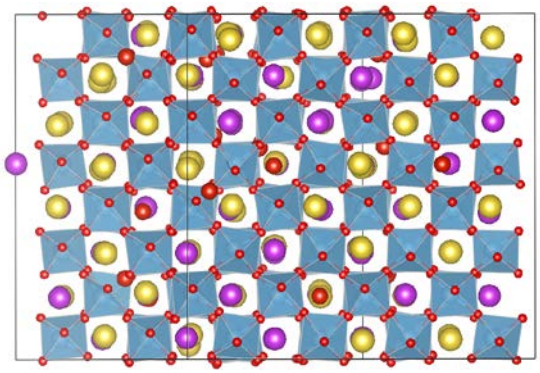

Fig. 2 Atomic configuration of $Na_{0.5}Bi_{0.45}TiO_{3-\delta}$ simulated by the RMC analysis. Yellow and purple spheres mean Na and Bi, respectively. Blue octahedra represent TiO_6.