MLF Experimental Report	提出日 Date of Report 2016/9/30
課題番号 Project No. 2015A0117 実験課題名 Title of experiment Pair distribution function analysis on oxide-ion distribution of $La_{9.33}Si_6O_{26}$-based oxide-ion conductor for an electrolyte of the solid oxide fuel cell 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 2016/2/29 - 2015/3/2 2015/3/25 - 2015/3/26

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: $La_{9.33+x}Si_6O_{26+1.5x}$
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

We prepared $La_{9.33+x}Si_6O_{26+1.5x}$ with different x contents by a hydrothermal method, and then identified the phases of the samples preliminarily by X-ray diffraction measurements. We also evaluated their metal compositions by the ICP atomic emission spectrometry.

For the purpose of defect-structure analysis, 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 mounted to a sample holder. The measurements were performed at room temperature for 3~4 hours. From the lattice constants and the metal compositions determined above, the Faber-Ziman structure factors $S(Q)$ were obtained, and then the $S(Q)$ were converted to reduced pair distribution functions $G(r)$. These data were analyzed on the basis of the Monte Carlo method, which is the so-called reverse Monte Carlo (RMC) technique.

Results

We refined crystal structures (unit cells) of $La_{9.33+x}Si_6O_{26+1.5x}$ by the Rietveld analysis using Bragg profiles, and then constructed simulation boxes for the RMC analysis. In the analysis, we applied an interatomic potential for Si-O bonds which was determined by the density functional theory (DFT) calculation using the quartz. Figures 1 and 2 show simulated patterns and an atomic configuration with 1512 atoms for the specimen with x=0, respectively. As seen in Fig. 1, we used the Bragg profile, the neutron $G(r)$, the neutron and the X-ray $S_{box}(Q)$ which were convolved considering the box size simultaneously, and the simulated patterns are well consistent with all the experimental data. From the atomic configuration (Fig. 2), it is indicated that the cavity volume around the La vacancy is larger than that predicted from the average structure. This may be due to repulsion between oxide anions around the cation vacancy.

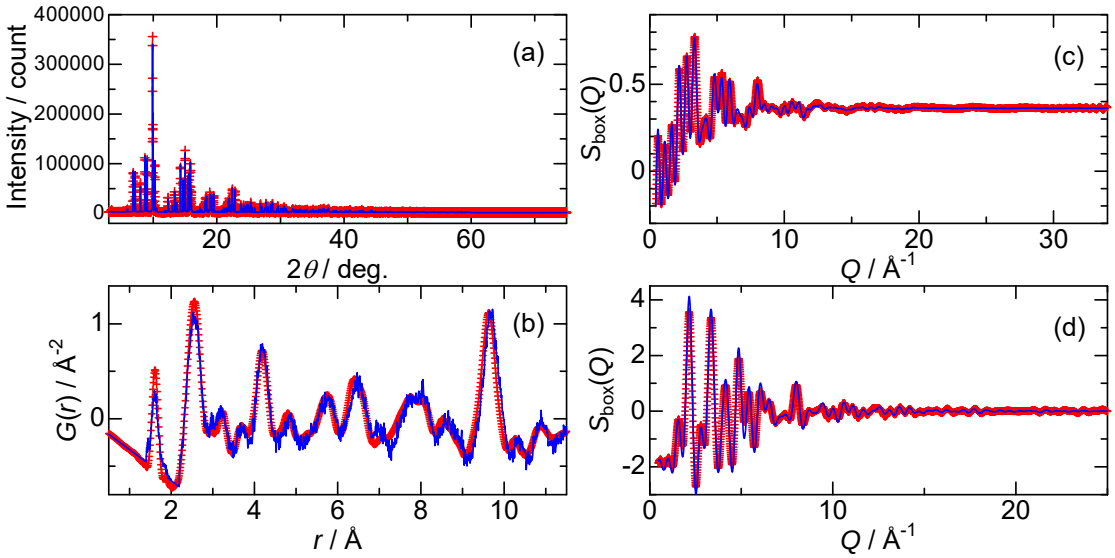

Fig. 1 (a) Bragg profile, (b) neutron $G(r)$, (c) neutron and (d) X-ray $S_{box}(Q)$ of $La_{9.33}Si_6O_{26}$. The red plus marks and the blue solid line represent the experimental data and RMC model, respectively.

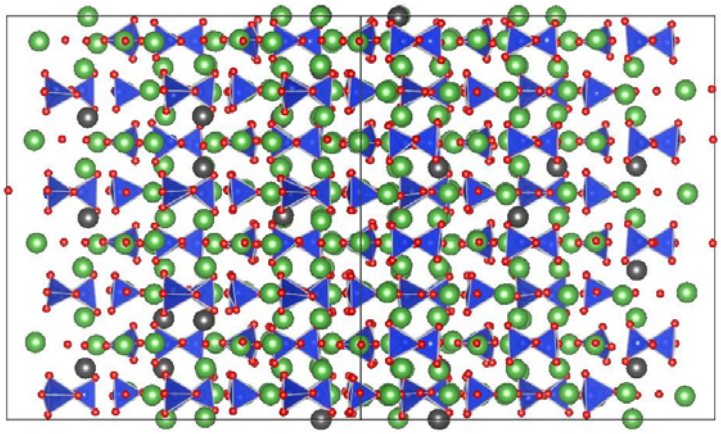

Fig. 2 Atomic configuration of $La_{9.33}Si_6O_{26}$ simulated by the RMC analysis. Green and gray spheres mean La and La vacancy, respectively. Blue octahedra represent SiO_4^{4-}, respectively.