MLF Experimental Report	提出日 Date of Report 2013/1/18
課題番号 Project No. 2012A0102 実験課題名 Title of experiment Effects of synthetic condition on crystal structure of $LaBaGaO_4$-based protonic 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 Takashi Kamiyama 装置名 Name of Instrument/（BL No.） SuperHRPD/BL08 実施日 Date of Experiment 2012/10/27 - 2012/10/29 2012/11/28 - 2012/11/30

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.

$La_{1-x}Ba_{1+x}GaO_{4-\delta}$, 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

$La_{1-x}Ba_{1+x}Ga_{1-y}Mg_yO_{4-\delta}$(x=0~0.1) were synthesized by conventional solid-state reaction and Pechini methods. Phases of the samples were identified by the powder X-ray diffraction measurements, and the metal compositions were evaluated with ICP measurements. As for these samples, conductivity measurements were carried out at intermediate temperatures, 400~800 ^oC, by an AC two probe method. Conduction species were estimated by measuring the conductivities as a function of partial pressures of water vapor and oxygen.

In order to clarify dependencies of the crystal structure on the composition and the synthetic process, neutron diffraction measurements were performed by SuperHRPD. In this experiment, powder of each sample with a weight of 1 g was heat-treated under H_2O- or D_2O-moisturized condition, and then was sealed into a V can. The can was mounted in the chamber, and then the diffraction pattern was recorded at room temperature with BS bank. The obtained data were analyzed based on the Rietveld method by using a Z-Rietveld program.

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

Results

Figure 1 and Table 1 show a Rietveld refinement pattern and refined structure parameters of $La_{0.9}Ba_{1.1}GaO_{4-\delta}$ synthesized by the Pechini method, respectively. In the analysis, a space group of the crystal structure was assumed as $P2_12_12_1$ (an orthorhombic structure), and atomic positions and displacement parameters of all the elements were refined. As shown in this figure, it was clarified that the sample had a single phase of the orthorhombic structure. It was also found that crystal structures of $La_{1-x}Ba_{1+x}Ga_{1-y}Mg_yO_{4-\delta}$ prepared by the other method and with other compositions of "x" were successfully refined as well.

From Table 1, it was indicated that an atomic displacement parameter, U_{iso}, of O3 was larger than those of the other oxygens. Based on our previous work using DFT calculation, proton tended to exist around the O3 site and then induce a local displacement at the site. Considering this, such a difference in the refined U_{iso} may reflect proton incorporation around the O3 site in the material. However, because these refinements could not determine proton's sites and occupancies, we will try a maximum-entropy method (MEM) analysis in near future.

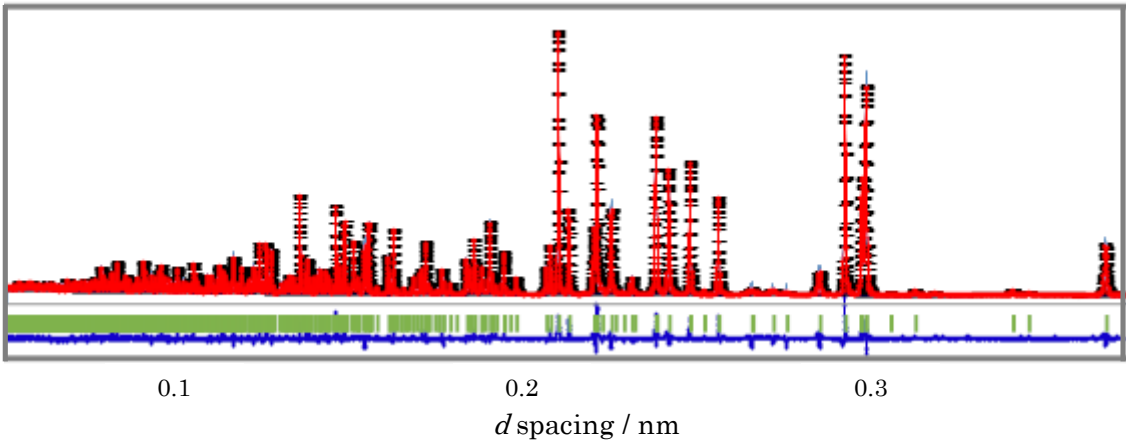

Fig. 1 Rietveld refinement pattern of $La_{0.9}Ba_{1.1}GaO_{4-\delta}$ (Pechini method). Dot marks show observed neutron diffraction intensities, and a solid line represents calculated intensities. Vertical marks indicate positions of Bragg refractions. A curve at the bottom is a difference between the observed and calculated intensities.

Table 1 Refined structure parameters of of $La_{0.9}Ba_{1.1}GaO_{4-\delta}$ synthesized by the Pechini method (S.G.. $P2_12_12_1$). *R*-factors were R_{wp}=7.92 % and R_p=5.85 %. Lattice constants were a=1.004744(6) nm, b=0.732666(3) and c=0.592883(2) nm.

Atom	Site	x	y	z	$10^4 \times U_{iso}(nm^2)$	Site occupancy
La1	4*a*	0.05032(5)	0.49705(7)	0.2354(1)	0.58(1)	0.9
Ba1	4*a*	=*x*(La1)	=*y*(La1)	=*z*(La1)	=*B*(Li1)	0.1
Ba2	4*a*	0.67184(8)	0.3338(1)	0.2394(2)	0.76(2)	1
Ga1	4*a*	0.33435(5)	0.27975(7)	0.2569(2)	0.70(1)	1
O1	4*a*	0.17571(7)	0.15360(9)	0.2442(2)	0.99(2)	1
O2	4*a*	0.4376(1)	0.1962(1)	0.4890(2)	1.55(2)	1
O3	4*a*	0.2901(1)	0.5030(2)	0.3778(1)	3.15(3)	1
O4	4*a*	0.4324(1)	0.2319(1)	0.0008(2)	2.15(3)	1