Study of Crystal Structure and Protonic Conduction Properties of $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ Prepared by Liquid Synthesis Method

Naoki HAMAO,^a Naoto KITAMURA,^{a,b,*} Naoya ISHIDA,^{a,b} Takashi KAMIYAMA,^c Shuki TORII,^c Masao YONEMURA,^c and Yasushi IDEMOTO^{a,b}

^a Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

^b Division of Ecosystem Research, Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

^c Institute of Materials Structure Science, High Energy Accelerator Research Organization, 203-1 Shirakata, Tokai, Ibaraki 319-1106, Japan

* Corresponding author: naotok@rs.tus.ac.jp

ABSTRACT

In order to investigate an effect of the preparation process on protonic conductivity of $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$, we attempt to prepare the samples with $x = 0.1$, $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$, by a liquid synthesis method as well as a conventional solid-phase method. Their electrical conductivities are measured from 300 to 900°C in various water vapor partial pressures, $P_{\text{H}_2\text{O}}$. From the result, it is found that the protonic conductivity is higher in the sample synthesized by the liquid synthesis method compared with that by the solid-phase method. In addition, it is also indicated that the $P_{\text{H}_2\text{O}}$ -dependence of the electrical conductivity around 600°C is more significant in the sample prepared by the liquid synthesis method. This result implies that this method enhances proton dissolution in $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ at least around the temperature range. To investigate a crystal structure change by the synthesis method, we perform powder neutron diffraction measurements. The Rietveld and maximum entropy method (MEM) analyses demonstrate that nuclear density of the proton is clearly observed between neighboring O3 sites, and suggest that the liquid synthesis method makes a site occupancy of proton higher.

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1. Introduction

Proton-conducting oxides have been attracting much attention because they can be applied for hydrogen devices such as the solid oxide fuel cell (SOFC), hydrogen sensors etc.^{1–5} Especially, the protonic conductors can be regarded as a promising candidate as an electrolyte for SOFC operating at intermediate temperature, i.e. around 500°C, which is so-called IT-SOFC. In contrast to widely-used SOFC using yttria-stabilized zirconia (YSZ) which is an oxide-ion conductor, the IT-SOFC with a protonic conductor has some advantages: for example, high usability of fuel, low cost and so on.^{6,7} At the moment, however, the proton-conducting oxides still have some problems for the commercial use.

Among the protonic conductors, oxides with the perovskite structure have been investigated actively in last few decades. BaZrO_3 -based materials can be considered as the most promising due to the high protonic conductivity, but it is difficult to fabricate their dense sintered bodies and this demerit makes the materials less attractive.^{8–11} From such background, other candidates for the electrolyte of IT-SOFC have been also proposed recently. For example, $(\text{La},\text{Sr})\text{P}_3\text{O}_9$ with a chain-type phosphate network, in which mobile protons are incorporated as defects for a charge compensation of Sr^{2+} for La^{3+} , is considered as interesting because it shows protonic conduction even under unhumidified condition.^{12–15} Unfortunately it is known that the electrical conductivity in a wet condition is lower in the phosphate compared with the barium zirconate, but it is noteworthy that a recent work indicated the increase of the Sr-substitution amount—in other words, proton concentration in the crystal—by applying a liquid phase method for the material preparation.¹⁶

Some researches also have devoted their efforts to LaBaGaO_4 -based protonic conductors with the $\beta\text{-K}_2\text{SO}_4$ -type structure, and have demonstrated that they exhibit protonic conductivity above $10^{-4}\text{ S}\cdot\text{cm}^{-1}$ at 500°C.^{17,18} In the case of $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$, a substitution of the lower cation (Ba^{2+}) to the La^{3+} site causes the oxygen-vacancy formation, and then the proton defects were produced in the crystal structure by incorporating ambient water vapor into the oxygen vacancy, according to the following defect equation and equilibrium:

where Ba'_{La} , H_2O , $\text{V}_\text{O}^{\bullet\bullet}$, $\text{O}_\text{O}^\times$, and $(\text{OH})_\text{O}^\bullet$ are Ba^{2+} replacing La^{3+} , water vapor, oxygen vacancy, O^{2-} at the O^{2-} site, and protonic defect, respectively. The interstitial protonic defect formed by Eq. (2) can be considered to contribute the electrical conductivity.

In this study, we aim to increase the protonic conductivities of $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$ by preparation with a liquid-phase method. For this purpose, $\text{La}_{1.1}\text{Ba}_{0.9}\text{GaO}_{4-\delta}$ was prepared by the Pechini synthesis method,¹⁹ and then the electrical conduction property was compared to that of a sample synthesized by a solid-state reaction. To examine a change of the crystal structure by the synthesis process, the crystal-structure analysis was performed using powder neutron diffraction. Based on these results, a relation between the structural change by the synthesis method and the conduction properties was discussed.

2. Experimental

2.1 Solid-state reaction method

La_2O_3 (99.99%, Wako Pure Chemical Industries, Ltd), BaCO_3 (99.9%, Wako Pure Chemical Industries, Ltd) and Ga_2O_3 (99.99%, Soekawa Chemical Co., Ltd) were used as starting materials. These materials were mixed for 2 h, and then the mixture was calcined at 1100–1200°C for 24 h in air with an intermediate grinding. The obtained powder was pressed into a pellet by a uniaxial pressing at 40 MPa, and then sintered at 1250°C for 12 h in air.

2.2 Liquid synthesis method

$\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$ was synthesized by means of the Pechini method. La_2O_3 , BaCO_3 and Ga_2O_3 were used as starting materials, and dissolved into a mixture of nitric acid and deionized water at 150°C. Citric acid (95%, Wako Pure Chemical Industries, Ltd) and ethylene glycol (99.9%, Wako Pure Chemical Industries, Ltd) were used as chelating and complexing agents, respectively. These agents were added to the above aqueous solution so that a molar ratio of metal: citric acid:ethylene glycol is 1:3:12, and the final solution was stirred at 150°C overnight. After that, the resulting gel was slowly dried and then esterized at 300°C. The obtained precursor was heat-treated at 650°C in air for 2 h, and then sintered at 1250°C in air for 12 h after uniaxial pressing at 40 MPa.

2.3 Characterization

Phase purity of synthesized samples, i.e. $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$ ($x = 0$ and 0.1), was investigated at room temperature by the X-ray diffraction (XRD) measurements with a graphite-filtered Cu K α radiation (45 mA, 45 kV) and a 2θ step of 0.02° (X'Pert Pro, PANalytical). In order to confirm the metal compositions, aqueous solutions of the samples were prepared using 6N-HCl and 30% H_2O_2 , and then analyzed by the inductively coupled plasma spectroscopy (ICP: ICPE-9000, Shimadzu). The particle morphologies of the calcined powders and the morphologies of the sintered pellets were observed by the scanning electron microscope (SEM: S-2600N, Hitachi High Technologies). The relative densities of the pellets were evaluated based on the Archimedes' principle.

Electrical conductivities were measured at 300–900°C under various water vapor partial pressures, $P_{\text{H}_2\text{O}}$, by the two-probe A.C. impedance method (LCR3532-50, HIOKI) using porous Pt as the electrodes. The $P_{\text{H}_2\text{O}}$ was controlled by bubbling O_2 gas through pure H_2O , saturated LiCl and MgCl_2 aqueous solutions at 30.0°C. In order to investigate the conduction species, the conductivities were also measured in D_2O atmosphere where the gas was moisturized by D_2O at 32.4°C, and then H/D isotope effects were discussed.

2.4 Crystal structure analysis

In order to clarify crystal structures, powder neutron diffraction patterns were measured at room temperature with SuperHRPD^{20,21} installed at J-PARC, Japan. For the neutron diffraction measurements, we prepared deuterated samples in which protons were replaced by deuterons in order to investigate protons' sites in detail. The deuteration was carried out by annealing the sample at 650°C under D_2O -moisturized O_2 gas. By using the data, crystal structures of the samples were analyzed based on the Rietveld method using Z-Rietveld program,^{22,23} and the nuclear density distributions were estimated by MEM analysis using Z-MEM.²⁴ These analytical results were visualized with VESTA.²⁵

3. Results and Discussion

3.1 Characterization

Figure 1 shows XRD patterns of $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$ ($x = 0$ and 0.1) prepared by the liquid-phase and solid-state methods. It is found that all the samples had the orthorhombic-type $\beta\text{-K}_2\text{SO}_4$ structure

Figure 1. X-ray diffraction patterns of $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$ obtained by each method. a) Solid state LaBaGaO_4 , b) Solid state $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$, c) Pechini method LaBaGaO_4 , d) Pechini method $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$.

Table 1. Lattice parameters calculated from XRD patterns of $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$ obtained by each method.

Sample	<i>a</i> /nm	<i>b</i> /nm	<i>c</i> /nm
Solid state LaBaGaO_4	1.0018(3)	0.7268(2)	0.5911(2)
Solid state $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$	1.0026(5)	0.7273(4)	0.5909(4)
Pechini method LaBaGaO_4	1.0037(3)	0.7248(2)	0.5905(4)
Pechini method $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$	1.0055(4)	0.7264(3)	0.5919(3)

Table 2. Analytical metal compositions of $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$ obtained by each method.

Sample	La	Ba	Ga
Solid state LaBaGaO_4	1.001(4)	1.0149(6)	0.985(6)
Solid state $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$	0.912(2)	1.095(6)	0.99(1)
Pechini method LaBaGaO_4	0.995(3)	1.007(2)	0.997(6)
Pechini method $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$	0.907(4)	1.1097(5)	0.9826(7)

(S.G. $P2_12_12_1$) although a tiny amount to $\text{LaBaGa}_3\text{O}_7$ was detected as a second phase only in $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ prepared by the Pechini method. Table 1 lists lattice parameters calculated from the XRD patterns by means of the least-squared method. As shown in this table, the lattice parameters were changed by the partial substitution of Ba for La, according to a difference in ionic radii of La and Ba [La^{3+} (VIII): 0.130 nm, Ba^{2+} (VIII): 0.156 nm].²⁶ Therefore, it can be considered that La site was occupied partially by the excess Ba. Moreover, in terms of an effect of the synthesis method, the lattice parameters of the $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ prepared by the Pechini method were larger compared with the specimen synthesized by the solid-state method. This result suggests that the crystal structure of the Ba-substituted material was changed by the synthesis process.

Table 2 shows the analytical metal compositions by ICP, which were calculated so that the sum of the metal compositions became 3. As a result, it is confirmed that the metal compositions were controlled well for all the samples.

Figures 2 and 3 show SEM images of the calcined particles and the morphologies of the sintered samples, respectively. The powder and grain sizes of the samples prepared by the Pechini method were

Figure 2. SEM images of calcined particles. a) Solid state $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$, b) Pechini method $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$.

Figure 3. SEM images of morphologies of sintered pellets. a) Solid state $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$, b) Pechini method $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$.

smaller than those obtained by the solid-state method. The densities were always above 95% of the theoretical density and thus the sintered pellets were dense regardless of the synthesis process, as shown in Fig. 3.

3.2 Electrical conduction property

3.2.1 H/D isotope effect on conductivity

The total electrical conductivities of the $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$ ($x = 0$ and 0.1) were measured under the $\text{H}_2\text{O}/\text{O}_2$ atmosphere, and the results are shown in Fig. 4. These values corresponded to

Figure 4. Temperature dependences of electrical conductivities under the $\text{H}_2\text{O}/\text{O}_2$ condition. ●: Solid state LaBaGaO_4 , ○: Solid state $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$, ■: Pechini method LaBaGaO_4 , □: Pechini method $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$.

the bulk conductivities essentially because the quite tiny contribution from the grain boundary could be observed only at the lower temperatures. In any synthesis methods, it is found that the electric conductivity was increased by the replacement of Ba in the La site. In order to investigate the conductive species, the electric conductivities were measured under $\text{D}_2\text{O}/\text{O}_2$ atmosphere for the Ba-substituted samples (Fig. 5). It is found that the conductivities under the $\text{D}_2\text{O}/\text{O}_2$ atmosphere were lower than those under the $\text{H}_2\text{O}/\text{O}_2$ atmosphere at the lower temperatures regardless of the synthetic method. This suggests that LaBaGaO_4 began to conduct protons at the temperature range by the partial substitution of Ba for La.

It is also noteworthy that the Ba-substituted sample synthesized by the Pechini method exhibited higher electrical conductivity than that prepared by the solid-state method at least in the investigated timescale. This suggests that the Pechini method is preferable as a synthetic process for the LaBaGaO_4 -based protonic conductor.

3.2.2 $P_{\text{H}_2\text{O}}$ -dependence of conductivity

As mentioned above, the $\text{La}_{1.1}\text{Ba}_{0.9}\text{GaO}_{4-\delta}$ shows protonic conduction significantly regardless of the preparation process. In order to investigate a change in the defect species as a function of temperature, the electronic conductivities of the samples were measured in atmospheres having various $P_{\text{H}_2\text{O}}$, which were controlled using saturated lithium-chloride and magnesium-chloride aqueous solution in addition to pure water. Figure 6 shows the $P_{\text{H}_2\text{O}}$ dependence of the conductivity of each sample. As shown in this figure, it is found that the conductivity of the $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ depended apparently on the $P_{\text{H}_2\text{O}}$ at lower temperature, and the dependency was more significant in the sample synthesized by the Pechini method. This implies a change in the protonic concentration by the synthetic route as discussed below.

In the case of the $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$, protonic defects are introduced through the equilibrium between the oxygen deficiency and ambient water vapor, which is expressed as Eq. (2) in the introduction section. According to this equation, higher $P_{\text{H}_2\text{O}}$ induces higher proton concentration and thus higher proton conductivity. Figure 7 summarizes the $P_{\text{H}_2\text{O}}$ dependence of the electrical conductivities and the H/D isotope effect, $\sigma(\text{H}_2\text{O})/\sigma(\text{D}_2\text{O})$. At higher temperature, the H/D isotope effects were not observed and the slopes of $\log \sigma$ versus $\log(P_{\text{H}_2\text{O}})$ were considerably small, indicating insignificant protonic conduction due to the negligible proton concentration. When the temperature decreased to below 650°C , however, the H/D isotope effect could be observed

Figure 5. Temperature dependences of electrical conductivities under the $\text{H}_2\text{O}/\text{O}_2$ (filled marks) and $\text{D}_2\text{O}/\text{O}_2$ conditions (open marks). a) Solid state $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$, b) Pechini method $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$.

and the slopes of $\log \sigma$ versus $\log(P_{\text{H}_2\text{O}})$ could not be ignored regardless of the synthesis method. In particular, the slope for $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ synthesized by the Pechini method was larger than that obtained by the solid-state synthesis, suggesting easy proton incorporation through Eq. (2) in the former sample. Because both the Ba-substituted specimens had essentially the same metal composition and the $\beta\text{-K}_2\text{SO}_4$ -type crystal structure, this observed phenomenon might be caused by the non-equilibrium situation for Eq. (2) due to the grain size and/or the inhomogeneous distribution of the constituent cations and defects within the grain. This indicates that the synthetic method does not affect the electrical conduction significantly if this material is used under sufficiently-high temperature, like in widely-used SOFC. However, lowering the operating temperature of SOFC may make such an effect by the synthetic process unignorable even for much longer timescale.

3.3 Crystal structure

3.3.1 Rietveld analysis

From the results of the section of 3.2, it is found that the protonic conduction properties were affected by the synthesis method. Because conduction properties are closely related to ionic diffusions in crystals and thus crystal structures,^{27–31} the prepared $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ were investigated with neutron diffractions in this study to clarify a change of the crystal structure by the preparation process.

Figure 6. $P_{\text{H}_2\text{O}}$ dependence of the conductivity of each sample. ●: Solid state $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$, ■: Pechini method $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$.

Figure 7. $P_{\text{H}_2\text{O}}$ dependence of the conductivity and the H/D isotopic effect of each sample. ●: Solid state $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$, ■: Pechini method $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$.

The collected data were analyzed by the Rietveld method and maximum entropy method (MEM). To get precise information of the proton site in the crystal, the samples were deuterated by the annealing treatment in advance.

As an example, Fig. 8 shows the Rietveld refinement pattern of the deuterated $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ prepared by the Pechini method, and the refined parameters and anisotropic atomic displacement parameters are given in Table 3 and Table 4, respectively. By assuming a single phase of the orthorhombic structure (S. G.: $P2_12_12_1$), the calculated diffraction pattern was in good agreement with the observed one. Table 5 summarizes the R values, which are indexes for goodness of fit, for the analytical results using structure models with and without deuteron in the crystal. Because a deuteron site of the specimen synthesized in this work is unknown, we applied the D site in literature³² as the initial value in the case of the analysis using the structure model with deuteron. As shown in Table 5, the R values became smaller, corresponding to better fitting, by assuming the D site in the crystal.

The refined crystal structure with deuteron for the deuterated $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ synthesized by the Pechini method is shown in Fig. 9. As shown in this figure, the D site was converged between the neighboring O3 sites. This site is well consistent with previously-reported proton position for $\text{La}_{0.8}\text{Ba}_{1.2}\text{GaO}_{4-\delta}$ and $\text{La}_{0.9}\text{Ba}_{1.1}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{4-\delta}$,^{27,32,33} and this result indicates that an average proton site in LaBaGaO₄-based materials is essentially independent of substitution species and concentration. Table 6

Figure 8. (Color online) Rietveld refinement patterns of deuterated $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ prepared by the Pechini method. +: Neutron diffraction intensities, —: Calculated intensities, |: Positions of the Bragg reflections, Bottom: Difference between the observed and calculated intensities.

Table 3. Refined structure parameters for deuterated $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ obtained by the Pechini method (S. G.: $P2_12_12_1$). Numbers in parentheses are estimated standard deviations of last significant digits, and parameters without deviations were fixed. $R_{\text{wp}} = 5.06\%$, $R_p = 3.84\%$ and $R_e = 3.08\%$. The refined lattice parameters were $a = 1.004708(6)$ nm, $b = 0.732648(4)$ nm and $c = 0.592888(3)$ nm.

Atom	Site	Site occupancy	x	y	z	$10^4 \times U_{\text{iso}} (\text{nm}^2)$
La/Ba2	4a	0.9/0.1	0.05019(5)	0.49635(9)	0.2398(2)	—
Ba1	4a	1	0.67128(9)	0.3336(1)	0.2459(4)	—
Ga	4a	1	0.33456(6)	0.27969(9)	0.2613(2)	—
O1	4a	1	0.17521(7)	0.1537(1)	0.2480(4)	—
O2	4a	1	0.4390(2)	0.2027(3)	0.4877(3)	—
O3	4a	0.831(5)	0.2909(2)	0.5024(4)	0.3852(3)	—
O4	4a	1	0.4305(1)	0.2259(2)	0.0010(3)	—
D	4a	0.054(4)	0.195(2)	0.500(4)	0.605(3)	0.3(5)

Table 4. Refined anisotropic atomic displacement parameters for deuterated $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ obtained by the Pechini method (S. G.: $P2_12_12_1$).

Site	$10^4 \times U_{11} (\text{nm}^2)$	$10^4 \times U_{22} (\text{nm}^2)$	$10^4 \times U_{33} (\text{nm}^2)$	$10^4 \times U_{12} (\text{nm}^2)$	$10^4 \times U_{13} (\text{nm}^2)$	$10^4 \times U_{23} (\text{nm}^2)$
La/Ba2	0.56(3)	0.99(3)	1.10(3)	−0.07(2)	−0.35(4)	0.27(7)
Ba1	0.53(4)	1.57(4)	0.94(4)	0.03(3)	0.010(7)	−0.45(6)
Ga	0.34(2)	1.18(3)	0.60(3)	−0.05(2)	0.20(4)	−0.26(6)
O1	0.33(3)	2.07(4)	2.00(4)	−0.56(3)	−0.28(7)	0.26(6)
O2	1.72(7)	4.91(9)	0.86(5)	−0.23(5)	−0.87(6)	0.91(6)
O3	1.34(6)	0.74(6)	1.19(5)	−0.05(5)	−0.45(3)	−0.42(5)
O4	1.47(6)	4.75(8)	0.64(4)	−0.54(5)	0.69(5)	−0.29(5)

shows the refined structure parameters of D site for each synthesis method. When the site occupancies of the D sites were compared, it is found that the Pechini method resulted in larger site occupancy than the solid-state method. This tendency can explain the effect

of the synthetic method on the protonic conductivity in the $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ mentioned above; i.e., the higher proton concentration may be one of the reasons why the sample preparation with the Pechini method resulted in higher protonic conductivity.

Table 5. R -factors of the refinements for $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$ obtained by each method.

		$R_{\text{wp}}(\%)$	$R_{\text{p}}(\%)$	$R_{\text{c}}(\%)$
Solid state	without D site	5.25	3.94	3.01
$\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$	with D site	5.22	3.92	3.01
Pechini method	without D site	5.15	3.89	3.08
$\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$	with D site	5.06	3.84	3.08

Figure 9. (Color online) Refined crystal structure of deuterated $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ prepared by the Pechini method.**Table 6.** Refined structure parameters for D site of $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ prepared by each synthesis method.

	Solid state $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$	Pechini method $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$
Site	$4a$	$4a$
x	0.198(7)	0.195(2)
y	0.50(2)	0.500(4)
z	0.60(1)	0.605(3)
$10^4 \times U_{\text{iso}} (\text{nm}^2)$	0.7(2)	0.3(5)
Site occupancy	0.013(4)	0.054(4)

3.3.2 Nuclear density distribution

In order to examine the D site in more detail, the nuclear density distribution was investigated by MEM analysis. In the analysis, we used two kinds of the structure model: i.e., the model with and without deuterium. Figure 10 shows the nuclear density distribution [3D and (020) plane] obtained by using both the models for the sample prepared by the Pechini method. Regardless of the structure model, nuclear density other than metals and oxygen was clearly observed around the O3 site, and the density was consistent with the D site optimized by the Rietveld analysis. This result demonstrates that the deuterium (proton) existed around the O3 site and formed a hydrogen bond with oxygens at the neighboring O3 sites. From the nuclear density distribution of (020) plane [in Figs. 10(c) and 10(d)], it is clearly observed that the nuclear density of the D site was spread between these O3 sites. This deuterium (proton) behavior may reflect one of the proton conduction pathways in the $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$. In the case of the sample synthesized by the solid-state method, the nuclear density distributions could not be detected clearly. This may be because the D site occupancy was lower as indicated by the Rietveld analysis.

Figure 10. (Color online) Nuclear density distributions of deuterated $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ prepared by the Pechini method. The analysis utilized the structure models without deuterium [(a) and (c)] and with deuterium [(b) and (d)]. The equi-density levels for (a) and (b) are 0.1 and 0.05 fm^{-3} , respectively. The densities on the (020) plane are presented in (c) and (d). The wR_{f} for (a) and (b) were 2.51% and 2.52%, respectively.

4. Conclusions

In this work, $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-\delta}$ -based protonic conductors were synthesized by the Pechini method in addition to the conventional solid-state reaction method. From the results of powder X-ray diffraction, it is confirmed that their main phase was the orthorhombic LaBaGaO_4 (S.G.: $P2_12_12_1$). It was also found that the lattice parameters of $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ were slightly larger in the sample prepared by the Pechini method than the solid-state method, suggesting that the crystal structure was affected by the synthesis method. As a result of the conductivity measurement, it is indicated that LaBaGaO_4 began to exhibit protonic conduction by substituting Ba for La partially regardless of the synthetic method, and the conductivity of the $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ prepared by the Pechini method was higher. From the $P_{\text{H}_2\text{O}}$ dependency of the conductivity, it is suggested that the proton concentration in the $\text{La}_{0.9}\text{Ba}_{1.1}\text{GaO}_{4-\delta}$ increased by the sample preparation with the Pechini method. The Rietveld analyses using neutron diffraction data also supported such a change in the proton concentration by the synthetic method. This structure change might be one of the reasons for higher proton conductivity in the sample prepared by the Pechini method. By the analysis based on the maximum entropy method, the nuclear density distribution of deuterium, corresponding to the proton site, was clearly observed between neighboring O3 sites.

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