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1. Introduction

To reduce environmental load and achieve high efficiency of energy usage, H2 energy devices such as a solid oxide fuel cell (SOFC) and a solid oxide electrolysis cell (SOEC) have attracted much attention in the last few decades. Especially, SOFC and SOEC using proton-conducting ceramics as electrolytes have possibility to work at intermediate-temperature range around 600°C.1-3 and thus are regarded as key devices for wide-spread use of H2 energy. As proton-conducting ceramics, Ba(Zr,Ce)O3-based materials with a perovskite structure have been investigated actively because of high proton conductivities, but they suffer from low sinterability, relatively poor chemical stabilities against acid gas like CO2.4 To overcome the problems, many researchers have devoted their effort to discover novel oxides with protonic conduction, and then some reports have found that LaBaGaO4 becomes to show protonic conduction at elevated temperature by substituting Ba2+ for La3+ and Mg2+ for Ga3+.5-12 Since La1-xBaxGa0.4-δO4 with x = 0.2 exhibits conductivities above 1 × 10-4 Scm-1 at 773 K under wet condition, LaBaGaO4-based materials can be regarded as one of the promising candidates as an electrolyte of a hydrogen energy device. At this moment, however, effects of substitution species on the proton conductivity have not been fully understood.

From such background, we investigated electrical conduction properties of La0.95M0.05BaGaO4-δ and La0.9Ba1.1Ga0.9-δO4-δ (M = Ba, Sr, and Ca) and La0.95M0.05BaGaO4-δ (M = Ga, Al, and In). We also studied crystal structures and electron-density distributions by a Rietveld refinement and a maximum-entropy method. As a result, it was found that a distortion of the crystal structure was the lowest in the Sr-substituted sample among La0.95M0.05BaGaO4-δ and became larger by the partial substitution for Ga. It was also suggested that both the Al and In substitutions deteriorated the conductivity. To clarify effects of the substitutions on crystal structures and electron-density distributions, we performed a Rietveld refinement and a maximum-entropy method. As a result, it was found that a distortion of the crystal structure was the lowest in the Sr-substituted sample among La0.95M0.05BaGaO4-δ and became larger by the partial substitution for Ga. It was also suggested that both the Al and In substitutions made (Ga, M)Oδ-BaOδ-AOδ rigid. Such structural changes by the partial substitutions could be considered to affect the electrical conduction properties.

1. Experimental

La0.95M0.05BaGaO4-δ (M = Ba, Sr, and Ca) and La0.9Ba1.1Ga0.9-δO4-δ (M = Ga, Al, and In) were synthesized by means of a conventional solid-state reaction method using La2O3, BaCO3, SrCO3, CaCO3, Ga2O3, Al2O3, and In2O3 as starting materials. These oxides were mixed with appropriate proportions, and were calcined at 1373 and then 1473 K. Pellets of the samples except for La0.95Ca0.05BaGaO4-δ were sintered at 1523 K for 12 h, and that of the Ca-substituted sample were sintered at 1623 K for 12 h. X-ray diffraction measurement (XRD: XPert Pro, PANalytical) and inductively coupled plasma atomic emission spectroscopy (ICP-AES: ICPE-9000, Shimadzu) were carried out for phase identification and metal-composition evaluation, respectively. Densities of the sintered pellets were investigated by scanning electron microscopy (SEM: S-2600N, Hitachi-High Tech.) and density measurements on the basis of the Archimedes’ principle. Electrical conductivities were measured under wet oxidizing condition (pH2O2 or pH2O = 4.2 kPa; pH2O = 0.01–100 kPa) at 400–850°C by a two-probe AC impedance spectroscopy in which electrodes were prepared by using Pt paste. The spectra were measured in a frequency range from 4.2 × 10 to 5 × 106 Hz. To investigate crystal structures and electron-density distributions of the samples, the synchrotron X-ray diffraction patterns were collected with a wave length of 0.05 nm by BL19B2 installed at SPring-8, Japan, and then the Rietveld refinements using the patterns were performed with a Rietan-FP program.13 Electron-density distributions were also analyzed by MEM with a Dynomia.14 These analytical results were visualized by a VESTA program.15

3. Results and Discussion

3.1 Characterization

Figure 1 shows XRD patterns of La0.95M0.05BaGaO4-δ (M = Ba, Sr, and Ca) and La0.9Ba1.1Ga0.9-δO4-δ (M = Ga, Al, and In) after the final sintering. It was confirmed from this figure that most of Bragg peaks could be attributed to the same crystal structure as pure LaBaGaO4 regardless of a substituent element although a tiny peak was observed around 28° in each sample. Table 1 lists the metal compositions estimated by ICP-AES. As can be seen in the table, the analytical compositions were essentially equal to the nominal values. To estimate densities of the sintered pellets, we performed density measurements on the basis of the Archimedes’ principle, and observed the morphologies by SEM although the
images are not shown here. As a result, it was demonstrated that all the pellets had relative densities of 96% or more and thus were sufficiently dense for electrical conductivity measurements.

### 3.2 Effect of dopant species on electrical conductivity

Figure 2(a) shows a Nyquist plot of the sample with M = Ba, i.e., La0.95Ba1.05GaO4-δ under an H2O-moisturized condition as an example. Since we could not distinguish resistances (conductivities) of the bulk and grain boundary as presented in this figure, only the total conductivity was discussed hereafter. Figure 2(b) shows electrical conductivities of the sample as a function of temperature. To confirm protonic conduction in the sample, the conductivities were measured under a D2O-moisturized condition as well [Fig. 2(b)]. The electrical conductivities in the H2O condition were very close to the values reported previously, and were higher than that in the D2O condition. In addition, the conductivity was almost independent of partial pressure of oxygen, as shown in Fig. 2(c).

Such a tendency indicates that the sample conducts protons (deuterons) which are incorporated into the crystal from ambient water vapor according to the following equation:

\[
\frac{1}{2} V^*_O + \frac{1}{2} H_2O(g) \rightarrow \frac{1}{2} O_2^{-} \Rightarrow OH^+_D
\]

Here, \(V^*_O\) represent oxygen vacancy which is generated by partial substitution with a lower-valent cation on the basis of an electro-neutrality principle. \(O_2^{-}\) and \(OH^+_D\) mean \(O^2-\) at the oxygen sites and interstitial proton coordinating to \(O^{2-}\). In the case of the LaBaGaO4-based materials, the proton might be regarded as HGaO4^+_D tetrahedron is formed in the materials. The proton diffuses throughout the crystal via a hydrogen bond by a hopping mechanism.

Moreover, it was supposed that the protonic conduction was significant especially at the lower temperatures since the conduc-
Electrochemistry, (in press)

![Electrochemistry, (in press)](image)

**Figure 3.** Temperature-dependences of electrical conductivities of (a) La$_{0.95}$M$_{0.05}$BaGaO$_4$ and (b) La$_{0.95}$Ba$_{1.1}$Ga$_{0.9}$M$_{0.1}$O$_4$. The parameters changed depending on diatomic radii between the host cations and the substituent cations, indicating the successful partial substitutions. In general, it is believed that a large lattice is preferable for protonic conductors, but this is not the case here. The Sr-substituted sample exhibited slightly lower conductivity than the Sr-substituted one [Fig. 3(a)] in spite of the smaller lattice volume. To discuss such a conductivity behavior based on crystal structures and electron-density distribution of these substituted samples.

**3.3 Effect of crystal structure and electron-density distribution on electrical conductivity**

As an example, Fig. 4 shows a Rietveld refinement pattern and a refined crystal structure of La$_{0.95}$Sr$_{0.05}$BaGaO$_4$, and Table 2 lists the refined structural parameters. By assuming the space group as $P2_1_2_1_2$, the refinement could be carried out successfully. It was found from Fig. 4(b) that all the oxygens tend to form GaO$_4$ groups although the oxygen sites are surrounded by La, Ba, and Ga sites. According to previous works, it can be considered that protons are incorporated into interstitial sites especially around the O3 site and diffuse via hydrogen bonds in the crystal. We also analyzed crystal structures of the other samples, and summarize the lattice parameters and volumes in Table 3. The parameters changed depending on diatomic radii between the host cations and the substituent cations, indicating the successful partial substitutions. In general, it is believed that a large lattice is preferable for protonic conductors. However, the Ba-substituted sample exhibited slightly lower conductivity than the Sr-substituted one [Fig. 3(a)] in spite of the larger lattice volume. To discuss structural features which have predominant influence on electrical conductivity of the LaBaGaO$_4$-based protonic conductors, we investigated distortion of (Ga, M')O$_4$ in detail. Table 4 presents quadratic elongations, $\alpha$, and bond-angle variances, $\sigma^2$, of the tetrahedra, defined as below:

$$\alpha = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{1}{l_i} \right)^2$$

$$\sigma^2 = \frac{1}{m-1} \sum_{i=1}^{m} (\phi_i - \phi_0)^2$$

In Eq. (2), $n$ and $l_i$ represent a number of bonds (i.e., 4) and a bond length, respectively, $l_0$ is a distance between a center and a vertex in a regular tetrahedron with the same volume. In Eq. (3), $m$ is a number of bond angles (i.e., 6), and $\phi_i$ and $\phi_0$ means a bond angle and an ideal bond angle (i.e., 109.28°) for a regular tetrahedron.

When we focus on La$_{0.95}$M$_{0.05}$BaGaO$_4$ (M = Ba, Sr, and Ca), the tetrahedral distortions of the Sr-substituted were lower than those of the others. Taking the ionic radii into account, it can be
considered that a large size mismatch between the host cation (La) and the substituent cation (M) induces large GaO₄ distortions because oxygens forming GaO₄ are also adjacent to the lanthanum site. Similar tendency can be also observed in the case of La₀.⁹₅Sr₀.₀⁵BaGa₀.₉M₀.₁O₄₋₄ (M = Ga, Al, and In) and La₀.⁹₅Ba₁.¹Ga₀.₉M₀.₁O₄₋₄ (M = Ga, Al, and In). The results are depicted in Fig. 5. As can be seen in this figure, electron density between (Ga, M)₀O₄ result in a rigid distortion suppressed proton dissolution expressed by Eq. (1) and lowered proton mobility.

Since the substitutions for the Ga site are considered to have significant effects on the protonic conduction directly according to discussion on Eq. (1), we also analyzed the electron-density distributions by MEM for the La₀.⁹Ba₁.¹Ga₀.⁹M₀.₁O₄₋₄ (M = Ga, Al, and In). The results are depicted in Fig. 5. As can be seen in this figure, electron density between (Ga, M)₀O₄ result in a rigid distortion suppressed proton dissolution expressed by Eq. (1) and lowered proton mobility.

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4. Conclusions

We investigated a relationship among electrical conduction properties, crystal structures, and electron-density distributions of LaBaGaO$_4$-based protonic conductors. As a result, it was found that the Sr substitution for La could enhance the electrical conductivity compared with both the Ca and Ba substitutions and that the partial substitutions for Ga made the conductivity worse. It was indicated from the crystal-structure analysis that the structural distortion was suppressed by substituting Sr for La whereas became larger by the partial substitution for Ga. It was also suggested that (Ga, M')O$_4$ tetrahedra became rigid by the Al and In substitutions. These structural changes can be considered to have influence on the electrical conduction properties of the LaBaGaO$_4$-based materials.

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