## Crystal and electronic structures of LaP<sub>3</sub>O<sub>9</sub>-based protonic conductors synthesized by liquid-phase method

<u>Naoto Kitamura</u><sup>1,2</sup>, Junpei Yamamoto<sup>1</sup>, Yasushi Idemoto<sup>1,2</sup>

 <sup>1</sup> Department of Pure and Applied Chemistry Faculty of Science & Technology, Tokyo University of Science,
<sup>2</sup> Division of Ecosystem Research,
Research Institute for Science and Technology, Tokyo University of Science,
2641 Yamazaki, Noda, Chiba 278-8510, Japan

#### **INTRODUCTION**

LaP<sub>3</sub>O<sub>9</sub>-based materials have drawn much attention as a protonic conductor at intermediate temperature range, i.e. around 600 °C, because they had high chemical stability and exhibited dominant protonic conduction even under dry condition <sup>1)</sup>. In recent years, many research tried to apply the materials to electrochemical devices, such as the solid oxide fuel cell (SOFC), but these trials were accompanied by some problems of the preparation process, which were basically originated from the thermal decomposition above 800 °C and the poor sinterability. In order to overcome these problems, it seems necessary to develop novel synthetic methods for these materials.

In this work, we synthesized  $La_{1-x}Sr_xP_3O_9$ powders by a liquid-phase method, and then investigated their phases and particle sizes. As for the sintered samples, we measured electrical conductivities as a function of water vapor and oxygen partial pressures. In order to study crystal and electronic structures in detail, the Rietveld and maximum entropy method (MEM) analyses using synchrotron X-ray diffraction data were also carried out.

### **EXPERIMENTAL**

La<sub>1-x</sub>Sr<sub>x</sub>P<sub>3</sub>O<sub>9</sub> with nominal compositions of x=0 and 0.03 were synthesized by a liquid-phase method. LaCl<sub>2</sub>•6H<sub>2</sub>O, SrCl<sub>2</sub>•6H<sub>2</sub>O and Na<sub>3</sub>P<sub>3</sub>O<sub>9</sub> were dissolved into distilled water, and then the pH of the aqueous solution was adjusted to about 1-2 by adding aqueous HCl. The solution was stirred at room temperature for 48 h, and then a precipitation was obtained. The powder was separated by filtration, washed with distilled water and finally dried at 60  $^\circ$ C. Afterward, the product was calcined at 700 °C for 10 h. These samples were identified by power X-ray diffractions (XRD), and the particle morphologies were evaluated by scanning electron microscopy (SEM) and particle-size distribution measurements. As for pellets sintered at 800 °C, the electric conductivities were measured by the AC impedance spectroscopy method from 300 to 700 °C as a function of partial pressures of water vapor and oxygen. H/D isotope effects on the conductivities were also examined in order to confirm protonic conduction. Crystal and electronic structures of these samples were analyzed in detail with synchrotron X-ray diffraction data, which were recorded at BL02B2 installed at SPring-8, Japan. In these analyses, the crystal structures were refined by the Rietveld technique (Rietan-FP), and the electron density distributions were visualized by the MEM (PRIMA).

#### **RESULTS AND DISCUSSION**

From XRD patterns, it was found that the obtained precipitates by the liquid-phase method described above were La<sub>1-x</sub>Sr<sub>x</sub>P<sub>3</sub>O<sub>9</sub>•6H<sub>2</sub>O. Particle sizes of the samples were estimated to be below 1 µm. After the calcination, they were decomposed to orthorhombic La<sub>1-x</sub>Sr<sub>x</sub>P<sub>3</sub>O<sub>9</sub> regardless of the metal composition (Fig. 1). We also measured electrical conductivities and H/D isotope effects of the sintered samples. As a result, it was demonstrated that the  $La_{0.97}Sr_{0.03}P_3O_9$  exhibited much higher conductivity than LaP<sub>3</sub>O<sub>9</sub> and showed clear H/D isotope effect: that is, the conductivity under D<sub>2</sub>O condition was lower than that under H<sub>2</sub>O condition. These results indicated that protons were incorporated into LaP<sub>3</sub>O<sub>9</sub> by substituting  $Sr^{2+}$  for La<sup>3+</sup> partially. Therefore, it can be concluded that the liquid-phase method proposed in this work prepared LaP<sub>3</sub>O<sub>9</sub>-based protonic conductors successfully.

the  $La_{1-x}Sr_xP_3O_9$ , we measured As for synchrotron X-ray diffraction patterns and then performed the Rietveld analysis. From the result, it was clarified that these materials could be attributed to an orthorhombic structure with a space group of  $C222_1$ , in which there are two P and five O sites crystallographically. It was also indicated that a distortion around P was dependent significantly on the crystallographic site. In order to reveal the origin of this difference, electron density distributions were analyzed by using the refined structure factors, and the result of La<sub>0.97</sub>Sr<sub>0.03</sub>P<sub>3</sub>O<sub>9</sub> is presented in Fig. 2. As shown in this figure, P and O formed strong P-O4 tetrahedron network in the crystal basically, but the oxygen at the O1 site, which is one of the bridged oxygens, has weaker bonds with the neighboring P at the P2 site. Such a bonding state might induce the difference in the distortion around each P site.



Fig. 1 X-ray diffraction patterns of  $(a)LaP_3O_9$  and  $(b)La_{0.97}Sr_{0.03}P_3O_9$  synthesized by the liquid-phase method.



Fig. 2 Electron density distribution of  $La_{0.97}Sr_{0.03}P_3O_9$  estimated by MEM.

# REFERENCES

1) K. Amezawa et al., Solid State Ionics, 176, 2867(2005).