Doped lanthanum polyphosphate (LaP\(_2\)O\(_9\)) exhibits relatively high proton conductivity. For the practical applications such as the electrolyte of fuel cells, however, its conductivity must be improved by 2 orders of magnitude. Protons are introduced into matrix by lower-valent cation doping, and proton conductivity depends on dopant species. To date, LaP\(_2\)O\(_9\) has been doped with only Ca, Sr and Ba. In this work, we tried to dope LaP\(_2\)O\(_9\) with Na\(^+\), K\(^+\), Mg\(^{2+}\) and Pb\(^{2+}\), as the new dopant species, due to their close ionic radii to La\(^{3+}\). Among them, only Pb could substitute for La at a comparable concentration to those of alkaline earth metals and its highest doping level was 6.4 mol\%(Doping level is defined as the concentration ratio of dopant (M) to host cation (La) site in matrix (nM/(La + M) × 100 (mol%)\)). Though Pb can exist as either divalent or tetravalent state, Pb in LaP\(_2\)O\(_9\) was identified to be divalent state by XPS analysis. Proton conduction was demonstrated by HD isotope effect. The electrical conductivity of Pb-doped LaP\(_2\)O\(_9\) increased with Pb-doping level, owing to the increase in proton concentration. The conductivity of 4.5 mol\% Pb-doped LaP\(_2\)O\(_9\) was about one order of magnitude lower than that of 7.9 mol\% Sr-doped LaP\(_2\)O\(_9\).

Several lanthanum phosphates exhibit pure and relatively high proton conductivity when doped with alkaline earth metals (e.g. La\(_2\)P\(_3\)O\(_9\),\(^4\) LaPO\(_4\),\(^5\)–\(^8\) and LaP\(_3\)O\(_9\).\(^6\)–\(^10\)). Additionally, they have high chemical stability at 200–500°C.\(^13\)–\(^14\) Owing to these excellent properties, they are regarded as prospective candidates for electrolytes in protonic ceramic fuel cells (PCFCs). Especially, lanthanum polyphosphate (LaP\(_2\)O\(_9\)) exhibits the highest conductivity among them (~10\(^{-4}\) S cm\(^{-1}\) at 400°C\(^16\)). For practical use, however, its conductivity must be increased by 2 orders of magnitude.

One of the problems preventing the conductivity enhancement is limited choices of dopant species. Proton conductivity is proportional to concentration and mobility of protons in matrix. Positive defects of interstitial protons are introduced into matrix to maintain electroneutrality, when negative defects are formed by lower valence cation doping.\(^5,16\) Thus, proton concentration depends on dopant species and increases with dopant concentrations, though dopant concentrations have upper limits which are different by dopant species.\(^5\) Proton mobility is also dependent on dopant species and dopant concentration. In fact, it has been previously reported that the conductivity of 1 mol\% Sr-doped LaP\(_2\)O\(_9\) is 1 order of magnitude higher than that of 1 mol\% Ca-doped LaP\(_2\)O\(_9\).\(^7\) This conductivity difference of LaP\(_2\)O\(_9\) indicates that proton concentration and/or proton mobility can be different by orders of magnitude, depending on dopant species. To date, however, LaP\(_2\)O\(_9\) has been doped with only Ca, Sr and Ba.\(^9\) In this study, new appropriate dopant species which can increase concentration and/or mobility of proton has been explored for further conductivity enhancement.

The new dopant species must be monovalent or divalent cations, because they must form negative defects by substituting for La\(^{3+}\). In addition, the doping levels comparable to those of alkaline earth metals should be attained (The highest value ever reported is 7.9 mol\% by Sr-doping\(^10\)). For achieving higher doping levels, the ionic radius of dopant is generally required to be similar to that of host cation. In light of this empirical rule, Na, K, Mg and Pb were selected as the candidates of the new dopant species in this work (La\(^{3+}\):1.16 Å, Na\(^+\):1.18 Å, K\(^+\):1.51 Å, Mg\(^{2+}\):0.89 Å, Pb\(^{2+}\):1.29 Å in eight-fold coordination\(^17\)). For the synthesis of doped LaP\(_2\)O\(_9\), precipitation method was employed, because it has several advantages over solid state reaction method (SSR) for enhancing the conductivity. For example, higher doping levels can be achieved.\(^10,18\) Additionally, larger and c-axis-oriented grains can be obtained,\(^19\) while grains are randomly oriented in the case of SSR. Larger grains reduce the density of grain boundary, which generally has an unignorable resistance against proton conduction, and c-axis orientation enhances the bulk conductivity, because c-axis has one of the highest conductivities in LaP\(_2\)O\(_9\) crystal.\(^10\)

**Charge Carrier Identification**

Monovalent or divalent cation-doping can introduce not only interstitial proton (H\(^+\)), but also oxygen ion vacancy (Vo\(^++\)) and electron hole (h\(^+\)).\(^12\) Since Vo\(^++\) and h\(^+\) can also function as charge carriers, electrical conductivity (\(\sigma\)) is given by the total of the three partial conductivities.

\[
\sigma = \sigma_{H^+} + \sigma_{O_2^-} + \sigma_h
\]

Here, \(\sigma_{H^+}\), \(\sigma_{O_2^-}\) and \(\sigma_h\) indicate the partial conductivities of proton, oxide ion and hole.

For the utilization as the electrolytes, the transport number of hole conduction must be ~0. In this work, these three partial conductions (especially hole conduction) have been discussed, by examining the partial pressure dependence and H/D isotope effect of electrical conductivity.

**Partial pressure dependence of conductivity**.— The concentrations of H\(^+\), Vo\(^++\) and h\(^+\) depend on water vapor and oxygen partial pressures (p\(_{H_2O}\) and p\(_{O_2}\)).\(^8\) Especially when the concentration of oxygen ion vacancy (C(Vo\(^++\))) can be regarded as constant (in other words, hydration level is low.), those of interstitial proton (C(H\(^+\))) and electron hole (C(h\(^+\))) depend only on p\(_{H_2O}\) or p\(_{O_2}\), and can be expressed as below.

\[
C(H^+) \propto (p_{H_2O})^{1/2}
\]
\[
C(h^+) \propto (p_{O_2})^{1/4}
\]

If the mobility of each carrier is independent on \(p_{H_2O}\) or \(p_{O_2}\), their partial conductivities are expressed as follows.

\[
\sigma_{H^+} \propto (p_{H_2O})^{1/2}
\]
\[
\sigma_{O_2^-} = \text{const.}
\]
\[
\sigma_h \propto (p_{O_2})^{1/4}
\]

Thus, the electrical conductivity also depends on \(p_{H_2O}\) and \(p_{O_2}\). By examining the partial pressure dependence of electrical conductivity, these conductivities can be deconvoluted.

**H/D isotope effect**.— Proton conduction can be verified also by examining H/D isotope effect on electrical conductivity. The conductivities of proton conductors in hydrogen atmosphere can be larger
pellets at 420 MPa. Though phosphate of tetravalent Pb was also tried to be prepared for a standard material, it could not be obtained.

Electrical conductivity measurement.—The electrical conductivity was measured by 2-probe AC impedance spectroscopy in humidified hydrogen atmosphere. For this measurement, ~200 µm thick of plate-like dense polycrystals of LaP3O9 were directly precipitated in phosphoric acid solutions. The obtained precipitates were held at 500°C in air for 100 hour to evaporate the remaining phosphoric acid, because it has been recently reported that the remaining phosphoric acid solutions can effect on the conductivity measurement. After that, Pt was deposited on the both sides of the plates as electrodes by sputtering using Eiko ion coater IB3. During the electrical conductivity measurements, humidified gas mixture of H2 and Ar was flowed over the samples. The equilibrium oxygen partial pressure (pO2) was controlled by changing pH2/pD2O ratio. pH2/D2O was varied from 3.2 to 31 kPa, by bubbling the gas through liquid water kept at appropriate temperatures. Especially for the isotope effect examination, pH2 and pD2O were kept at 5.0 kPa, by bubbling the gas through liquid water or deuterium water, kept at 33 ± 3°C, respectively.

Results and Discussion

The following abbreviations are used in this text. Cinit is the initial concentration ratios of dopant to La in phosphoric acid solutions (≡M/(La + M) × 100, in solutions). LP(Minit) is x mol% M-doped LaP3O9. For example, 5 mol% Pb-doped LaP3O9 is LP(Pb5).

Exploration of new dopant species.—In this experiment, the reagents were mixed at the ratio of La:M:P = 0.9:0.1:15 or 0.8:0.2:15 (Cinit = 10 or 20) and LaP3O9 was precipitated at 230°C in air. The powder X-ray diffraction patterns of the obtained precipitates are shown in Fig. 1. Single-phase LaP3O9 precipitated from every solution in the case of Cinit = 10, while the secondary phases of NaLa(PO3)4 or MgP2O6 precipitated with LaP3O9 from Na or Mg-containing solutions, in the case of Cinit = 20. Therefore, the upper limits of Cinit for obtaining single phase LaP3O9 lie between 10 and 20 for Na- and Mg-containing solutions. In the case of K-containing solutions, the upper limit is larger than 20, but it might be of the same order as that for Na-containing solutions because Na and K are both alkali metals and the existence of KL(PO3)4 has also been reported. The upper limit for Pb-containing solutions will be discussed later.

The concentrations of Mg, K and Pb on the surface of single-phase LaP3O9 precipitates were analyzed by EDX, and that of Na was analyzed by WDX. Pb was detected from the precipitate and its local concentration was varied from 0.7 to 6.4 mol% (the error was defined as twice the standard deviation). Na doping level is considered to be ~1 mol% at most. Thus, only Pb can substitute for La in LaP3O9 at a considerable doping level, among Na, K, Mg and Pb.

Achievable doping level of Pb.—In this experiment, the reagents were mixed at the ratio of (La + Pb):P = 1:15 (Cinit = 0–60), and LaP3O9 was precipitated at 230°C in air. The powder X-ray diffraction patterns of the obtained precipitates are shown in Fig. 3. When Cinit was small (Cinit ≤50), single-phase LaP3O9 precipitated, while the secondary phase of PbP2O6 precipitated with LaP3O9 when Cinit was larger (Cinit = 60). The compositions of single phase LaP3O9 were analyzed by ICP-AES (Fig. 4). The Pb-doping level tends to increase with Cinit, and reached to 6.4 mol% at Cinit = 50. Though slightly higher Pb-doping levels may be achieved in the range of 50 < Cinit < 60, Pb-doping level of 6.4 mol% is as high as the maximum Sr-doping level ever reported (7.9 mol%).

Valence determination of Pb in LaP3O9.—Comparing the XPS spectra of PbP2O6 and Pb-doped LaP3O9 (Fig. 5), the binding energies of Pb 4f 5/2 and 4f 7/2 were accurately matched (144 eV, 139 eV respectively). Based on this result, the valence of Pb in LaP3O9 matrix

### Table I. Starting materials for synthesis.

| Material       | Purity | Manufacturer                      |
|----------------|--------|-----------------------------------|
| H3PO4          | 85%    | Nacalai Tesque                    |
| La2O3          | 99.9%  | Nacalai Tesque or Shin-Etsu Chemical |
| NaHCO3         | 99.8%  | Nacalai Tesque                    |
| KHCO3          | 99.5%  | Nacalai Tesque                    |
| MgO            | 99.9%  | Wako Pure Chemical Industries     |
| PbO            | 99%    | Nacalai Tesque                    |

Characterization.—Phase identification was carried out at room temperature via X-ray diffraction (XRD) analysis on PANalytical X’Pert-Pro MPD using Cu-Kα radiation. The lattice volume was determined by the Rietveld method using X’Pert HighScore Plus software (Version 2.2c). The morphology of precipitates was observed using KEYENCE VE-7800 scanning electron microscopy (SEM).

The compositions of the precipitates were analyzed by energy dispersive X-ray Spectroscopy (EDX) on EDAX Genesis XM2, Wave-length dispersive X-ray Spectroscopy (WDX) on Microspec WDX-3PC or inductively coupled plasma atomic emission spectrometry (ICP-AES) on Seiko Instruments SPS3500. An accelerating voltage of 20 kV was used during EDX and WDX analyses. As the standard materials of WDX analysis, NaP04 (95%, Wako Pure Chemical Industries) and undoped LaP3O9 were used. Undoped LaP3O9 was precipitated at 250°C from a phosphoric acid solution with a composition of La:P = 0.8:15. It has been reported that the doping level of Sr-doped LaP3O9 synthesized by precipitation method depends on precipitation period. Thus, doping levels in LaP3O9 were derived from the average compositions of whole precipitates analyzed by ICP-AES.

Valence determination of Pb was carried out at room temperature via X-ray photoelectron spectroscopy (XPS) analysis on JEOL JPS-9010TRX using Mg Kα radiation. The spectrometer was calibrated using the photoemission line C 1s (binding energy 285.0 eV). As a standard material, PbP2O6 (phosphate of divalent Pb) was precipitated from phosphoric acid solution, by mixing the reagents at the ratio of Pb:P = 1:5:15 and setting the precipitating temperature at 270°C. The obtained precipitates were ground into powder, and pressed into
Figure 1. Powder X-ray diffraction patterns of precipitates from phosphoric acid solutions containing (a) Na, (b) K, (c) Mg or (d) Pb. There were several unknown peaks (∼22.2°, ∼33.2° etc.) in the powder X-ray diffraction pattern of the precipitate from Na-containing solution of C_{init} = 20, and in that from Mg-containing solution of C_{init} = 20, the diffraction peaks attributed to MgP₂O₆ can be observed at ∼19.5° and ∼28°.

should be the same as that in PbP₂O₆, i.e. +2. However, this result might not be conclusive, because the binding energies of tetravalent Pb in phosphates are not available.

In order to support the result of XPS analysis, the lattice volumes of undoped and Pb-doped LaP₃O₉ are discussed (Fig. 6). The lattice volume increased with Pb-doping level. The ionic radius of Pb⁴⁺ is smaller than that of La³⁺, while that of Pb²⁺ is larger (Table II). If Pb existed as Pb⁴⁺ in LaP₃O₉ matrix, the lattice volume would decrease as Pb-doping level increased. Therefore, this result confirms that the valence of Pb is +2 in LaP₃O₉.

Electrical conductivity.— Morphology of plate-like dense polycrystals.—For conductivity measurement, plate-like dense polycrystals of undoped and Pb-doped LaP₃O₉ were directly precipitated from phosphoric acid solutions. The reagents were mixed at the ratios shown in Table III. All of the dense polycrystals were single-phase LaP₃O₉ (Fig. 7a). Their Pb doping levels and relative densities are also shown in Table III, and their relative densities were over 97%.

It was previously reported that the plate-like polycrystals of Sr-doped LaP₃O₉ had two geometrically different surfaces, upper surface and lower surface. Upper surface is the plane facing to the solutions during the precipitation, and consists of large columnar grains (∼100 μm). Since the columnar grains are unidirectionally crystallized along c-axis, (001) planes tends to be oriented parallel to upper surface. In contrast, lower surface (facing to the bottom of the crucibles) consists of relatively smaller grains (∼20 μm), and (110) planes tended to be oriented parallel to this surface.

Pb-doped LaP₃O₉ also followed the above characteristics. Orientation can be determined from Fig. 7b and 7c, and grain size can be measured using Fig. 8. Additionally, as Pb doping level increased,
Figure 3. Powder X-ray diffraction patterns of the precipitates from the solutions containing various concentrations of Pb. The patterns of $C_{\text{init.}} = 10$ and 20 are the same as those shown in Fig. 1.

Figure 4. The dependence of Pb-doping level in LaP$_3$O$_9$ on the concentration ratio of Pb to La in solutions.

Figure 5. XPS spectra of PbP$_2$O$_6$ and Pb-doped LaP$_3$O$_9$. Pb-doped LaP$_3$O$_9$ was precipitated at 230°C from phosphoric acid solutions with a composition of La:Pb:P = 0.8:0.2:15. Though the composition of Pb-doped LaP$_3$O$_9$ precipitate has not been analyzed by ICP-AES, its Pb doping level is considered to be ∼3.3 mol%, based on the initial composition of the solution.

Figure 6. The dependence of lattice volume of LaP$_3$O$_9$ on Pb-doping level. Filled and open symbols represent the lattice volumes of single-phase LaP$_3$O$_9$ precipitated in air (samples used in the section Achievable doping level of Pb) and those precipitated in humidified air (dense polycrystals for electrical conductivity measurement detailed in the section Morphology of plate-like dense polycrystals) respectively.

(001) planes were more strongly-oriented parallel to upper surface, and were almost completely-oriented when Pb doping level is larger than 2.9 mol% (Fig. 7b).

Impedance spectrum.—The impedance spectrum of LP(Pb4.5) is shown in Fig. 9 as a typical example. In the spectrum, there were one clear large arc and unclear arc at low frequency range. The diameter of the large arc was almost independent on hydrogen partial pressure ($p_{H_2}$), and its electric capacitance was calculated to be $\sim 10^{-11}$ F. Based on $p_{H_2}$-independence, this arc is not attributed to the reaction impedance at the interface between electrolyte and electrode. Then, it should be attributed to either bulk impedance or grain boundary-impedance. In the case of typical ionic conductor of yttria-stabilized zirconia, the capacitances of the arcs attributed to bulk and grain boundary are reported to be $\sim 10^{-12}$ F and $\sim 10^{-9}$ F respectively (Section 4.1.3 in Reference 23). Thus, the large arcs in Fig. 9 should be attributed to bulk impedances. The arc attributed to the grain boundary impedance would be too small to be seen, due to the relatively low density of grain boundary (see Fig. 8). Thus, the bulk conductivity can be regarded as the total conductivity, in the case of this sample.

Charge carrier identification.—In the cases of LaP$_3$O$_9$ doped with alkaline earth metals, their electrical conductivities depend on neither $p_{H_2O}$ nor $p_{O_2}$, but show H/D isotope effect. $p_{O_2}$-independence indicates a negligible transport number of hole conduction, and the isotope effect indicates a considerable transport number of proton conduction, though the cause of $p_{H_2O}$-independence has never been clarified. In this manner, LaP$_3$O$_9$ doped with alkaline earth metals are verified to be an ionic conductor with a considerable transport number of proton conduction. In isotope effect examination, however, one must consider a possibility that if a material has hole conductivity, its electrical conductivity might be different between hydrogen and deuterium atmospheres, depending on the equilibrium oxygen partial pressure. Thus, with considering that possibility, the partial pressure dependence and isotope effect of electrical conductivity of Pb-doped LaP$_3$O$_9$ were examined.

Table II. The ionic radii of the several cations in eight-fold coordination.17

| Cation | Ionic radius / Å |
|--------|-----------------|
| Pb$^{2+}$ | 1.29 |
| La$^{3+}$ | 1.16 |
| Pb$^{4+}$ | 0.94 |
As shown in Fig. 10a and 10b, the electrical conductivity of LP(Pb4.5) depends on neither $p_{H_2O}$ nor $p_{O_2}$. Additionally, as shown in Fig. 10c, the conductivity in hydrogen atmosphere was $\sim$1.08 times higher than that in deuterium atmosphere. Since the conductivity in hydrogen atmosphere was clearly higher even when $p_{O_2}$ was similar (Fig. 10b), the conductivity difference in isotope effect examination should be attributed to the difference in charge carrier ($H^+$/D$^+$).

![Figure 7](image1)

**Figure 7.** X-ray diffraction patterns of (a) ground powders, (b) upper surfaces and (c) lower surfaces of plate-like dense polycrystals.

![Figure 8](image2)

**Figure 8.** The SEM images of plate-like dense polycrystals of undoped and Pb-doped LaP$_3$O$_9$. The Pb-doping levels and thicknesses of them are shown in this figure.

![Figure 9](image3)

**Figure 9.** The impedance spectra of LP(Pb4.5) at 400 $^\circ$C in humidified hydrogen atmosphere ($Ar-x$ kPa $H_2$-3.2 kPa $H_2O$, $x = 10, 30, 98$).

| Initial compositions of solutions, doping levels and relative densities of plate-like dense polycrystals of LaP$_3$O$_9$. Theoretical density was derived from the lattice volume calculated by Rietveld method and the formula weight in which Pb substitution was taken into account. |
|---|---|---|---|---|
| Sample | La | Pb | P | $C_{\text{mix}}$ | Doping level/mol% | Relative density/% |
| Undoped | 0.8 | 0 | 15 | 0 | 0 | 100 |
| Pb-doped | 0.8 | 0.042 | 5 | 1.1 | 98 |
| | 0.8 | 0.089 | 10 | 1.7 | 97 |
| | 0.8 | 0.2 | 20 | 2.9 | 98 |
| | 0.7 | 0.18 | 20 | 3.5 | 97 |
| | 0.7 | 0.47 | 40 | 4.5 | 97 |
Therefore, Pb-doped LaP₃O₉ should be an ionic conductor with a considerable transport number of proton conduction.

Dependence of conductivity on Pb doping level.—The bulk conductivities of undoped and Pb-doped LaP₃O₉ are shown in Fig. 11. The conductivities proportionally increased with the Pb doping level. This conductivity enhancement could be associated with the increase in the proton concentration and/or in orientation strength of grains along c-axis (as mentioned in Morphology of plate-like dense polycrystals section). If it was mainly associated with the increase in orientation strength, the conductivities should have been almost constant when Pb doping level was larger than 2.9 mol%, since (001) planes were almost completely-oriented parallel to upper surfaces in that range of doping level. However, the conductivity clearly increased linearly even in that range. Therefore, the conductivity was enhanced mainly by the increase in the proton concentration, which is caused by the increase in Pb doping level. It should be noted that, in the plate-like polycrystals of Pb-doped LaP₃O₉, small gradients of Pb doping level was seen along the direction normal to the surfaces. In the case of LP(Pb3.5), for example, local Pb doping level varied from 1.4 mol% to 5.0 mol%. However, we estimated the effect of the doping level gradient on the apparent conductivity and found that the deviation of the apparent conductivity from that of the ideally homogeneous sample was only 10–20%.

Temperature dependence of the conductivity.—The temperature dependence of the conductivity of LP(Pb4.5) was investigated in the range of 200-400 °C (Fig. 12). In that temperature range, the activation energy of LP(Pb4.5) was calculated to be 0.79 eV, and larger than that of LP(Sr7.9) prepared in the similar manner (0.67 eV). The conductivity of LP(Pb4.5) was about one order of magnitude lower than that of LP(Sr7.9), even though the doping level was only twice lower. Since these two samples have the similar morphologies, the difference in conductivity is not attributed to that in morphology, but to those in proton concentration and/or proton mobility in LaP₃O₉ matrix.

Summary

In this study, it was demonstrated that LaP₃O₉ can be doped with Pb at a doping level of 6.4 mol%, comparable to those of alkaline earth metals. Pb substituting for La in LaP₃O₉ matrix was identified to be divalent by XPS, and it was confirmed by the lattice volume change induced by Pb doping. It was also revealed that Pb-doped LaP₃O₉ is
an ionic conductor with a considerable transport number of proton conduction. Its electrical conductivity increased with Pb doping level. This trend can be attributed mainly to increase in the proton concentration, rather than to increase in the orientation strength of grains. As far as the authors know, this is the first time for proton conduction to be exhibited by Pb doping, in proton-conducting phosphates. Unfortunately, the result of electrical conductivity measurement implied that Pb doping reduce proton concentration and/or proton mobility in LaP₃O₉ matrix, compared to Sr doping. However, it should still be worth trying to dope other rare earth containing materials with Pb for the conductivity enhancement.

Acknowledgments

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