Oxide Ion Conduction in the Perovskite-type LaY\textsubscript{2}O\textsubscript{3} Doped with ZrO\textsubscript{2}

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Received June 25, 2010; Accepted August 22, 2010

In order to find a new type of oxide ion conductor, the electrical conduction was measured in the substituted perovskite-type oxides. In the present case, LaY\textsubscript{2}O\textsubscript{3} was used as a based material with an orthorhombic and comparatively large unit cell, and a novel substitution method was introduced to intend to increase the concentration of oxide ions, e.g., La\textsubscript{1-x}Y\textsubscript{x}O\textsubscript{3+2x/2}. As a result, the LaY\textsubscript{2}O\textsubscript{3}-based perovskite-type solid solution was found to be formed, where the enhanced oxide ion conduction was observed as compared with that of the based material. A typical sample was La\textsubscript{0.5}Y\textsubscript{1.5}Zr\textsubscript{0.5}O\textsubscript{2.5}, the ionic conduction of which was 1.2 × 10\textsuperscript{-2} S cm\textsuperscript{-1} at 1000 °C. Another substitution method of La\textsubscript{1-x}Zr\textsubscript{x}YO\textsubscript{2+2x} resulted in the analogous result. Considering these results and the further structural and density measurements, the charge carriers in these phases were expected to be due to interstitial oxide ions.

Key Words: Oxide Ion Conductor, Interstitial Oxide Ion, Perovskite-type, Lanthanum Yttrium Oxide

1 Introduction

The stabilized zirconias are well-known as typical high temperature-type oxide ion conductors. These high oxide ion conducting solids are potentially useful for electrolyte materials of the solid oxide fuel cell (SOFC) and oxygen gas sensor. The perovskite- and pyrochlore-type oxides are also familiar to form typical groups of oxide ion conductors.\textsuperscript{1,4} In most conductors, oxide ion vacancies usually contributed to the oxide ion conduction. Besides these oxides, several new oxide ion conductors showing the special crystal structure have recently been reported.\textsuperscript{5,7} The authors have been also exploring new ionic conductors and have reported high oxide ion conduction in the scheelite-type oxides such as PbWO\textsubscript{4},\textsuperscript{8,9} where the interstitial oxide ions played very important roles for oxide ion movement on behalf of oxide ion vacancies.\textsuperscript{10,11}

PbWO\textsubscript{4} generally has a crystal structure corresponding to deformed fluorite. The ionic lattice clearance formed by the distortion would permit creation of excess oxide ions and the subsequent oxide ion migration in case higher valence cations were substituted for the lead sites. Considering this fact, if it were possible to put oxide ions by higher valence cation doping in the perovskite-type oxide having fairly wide lattice clearance, we might be able to observe the oxide ion conduction \textit{via} interstitial oxide ions in the resultant perovskite-type oxide solid solution. Descriptions of interstitial oxide ions sometimes appeared in technical papers describing the electrode catalysis of SrTiO\textsubscript{3}-based anode material for SOFC.\textsuperscript{12} However, the obvious oxide ion conduction property \textit{via} interstitial oxide ions in the perovskite-type oxide except some compounds such as K\textsubscript{2}NiF\textsubscript{4}-type oxides\textsuperscript{13-15} remained unknown.

In our laboratory, LaY\textsubscript{2}O\textsubscript{3} was chosen as a based material to check the oxide ion conduction by interstitial ions at first, because it has a distorted perovskite-type structure (tolerance factor, \( t = 0.85 \)) and denoted by GdFeO\textsubscript{3}-type\textsuperscript{16} and considerably larger lattice constants (\( Pm\text{na}_2 \_2 \) : \( a = 6.052 \) Å, \( b = 5.936 \) Å, \( c = 8.511 \) Å, \( Z = 4 \))\textsuperscript{7} due to large ionic radii of La\textsuperscript{3+} (1.36 Å [12-fold coordination]) and Y\textsuperscript{3+} (0.90 Å [6]).\textsuperscript{18} This structure is also known as an orthorhombic phase, which is the low temperature form of LaY\textsubscript{2}O\textsubscript{3} stable below 1450 °C.\textsuperscript{19,21} In order to increase the oxygen contents, tetravalent or higher valence metal cation should be doped to the lanthanum or yttrium sites. However, valence-changeable cation could not be doped to check the excess oxide ions or interstitials. Here, Zr\textsubscript{2}O\textsubscript{4} was the first candidate for the substitutes, and the solid solution formation range and its electrochemical properties were investigated in the substituted system. In the present paper, we show the oxide ion conduction in the Zr-substituted perovskite-type oxides phases as a prompt report.

2 Experimental

The samples were prepared from reagent grade powders of La\textsubscript{2}O\textsubscript{3} (Wako Pure Chemical Ind., 99.99 %), Y\textsubscript{2}O\textsubscript{3} (Wako, 99.9 %) and Zr\textsubscript{2}O\textsubscript{4} (Tosoh, TZ-0). The required quantities of reagents were mixed thoroughly in an agate mortar and fired at 1100 °C in air for 10 h. Thereafter the samples were finely ground, pressed into cylindrical pellets (5 mm diameter by 8 to 10 mm length) and discs (12 mm diameter by 2 to 3 mm thickness) under a pressure of 2 × 10\textsuperscript{5} kg cm\textsuperscript{-2} and sintered again at 1450 °C.

The crystal phase of sintered samples was identified by X-ray diffraction using Ni-filtered copper radiation (Shimadzu, XRD-6000 diffractometer). The density of a few powder samples was measured by the He-pycnometer (Yuasa Ionics, Multipycnometer). The electrical conductivity was measured by the two-probe ac method (HP-4192A) for cylindrical samples, both flat faces of which were coated with porous platinum paste as the electrodes. Although the impedance plots were used for
Results and Discussion

In the first case, the samples in which Zr$^{4+}$ was doped to the Y$^{3+}$ sites in LaYO$_3$ was investigated, because Zr$^{4+}$ has the ionic radius of 0.72 Å [6] near to that of Y$^{3+}$ (0.90 Å [6]) than La$^{3+}$ (1.36 Å [12]). The oxide samples obtained was white-colored throughout the total composition, and densely sintered so as not to absorb organic solvents contained in the platinum paste electrode material in the next experiment. The sample relative densities were estimated to be higher than 93% from the sample dimensions and weights.

Powder X-ray diffraction patterns of representative samples shown by LaY$_{1-x}$Zr$_x$O$_{3+y/2}$ are indicated in Fig. 1. Pure LaYO$_3$ shows a diffraction pattern coinciding with the JCPDS data (No. 09-0032) of a perovskite-type orthorhombic phase. The samples of x ≤ 0.05 show the similar diffraction patterns. For the samples of x ≥ 0.075, however, some extra peaks appeared indicating coexistence of the second phase in the orthorhombic one. In this system, the limiting composition to show the perovskite-type solid solution formation is near x = 0.50, which would make some excess oxide ions in a unit cell.

Representative Arrhenius plots of conductivity measured in air are shown in Fig. 2. For pure LaYO$_3$, the conductivity is 5.8 × 10$^{-4}$ S cm$^{-1}$ at 1000 °C. Enhanced conductivities are observed in the samples substituted by zirconium. By comparison at the same temperature, the conductivity once increases but somewhat decreases in the narrow solid solution range up to x = 0.05. At 1000 °C, the highest conductivity is observed in the x = 0.025 sample (σ = 1.2 × 10$^{-2}$ S cm$^{-1}$).

In order to investigate the nature of the charge carriers in these conductors, oxygen gas concentration cells were constructed using sample discs as electrolytes and the cell EMFs were measured (Fig. 3). The measured EMFs, $E$, of LaYO$_3$ are somewhat lower that the theoretical values from the Nernstian equation, $E_0$. Considering no stable EMF was observed at temperatures lower than

![Fig. 2](image_url) Representative Arrhenius plots of conductivity measured in air for LaY$_{1-x}$Zr$_x$O$_{3+y/2}$.

![Fig. 3](image_url) EMFs of the oxygen gas concentration cells constructed using sample discs as electrolytes. The cathode gas and anode gas were 1 atm oxygen and air, respectively. Dotted line shows the theoretical EMFs calculated by the Nernstian equation of $E = RT/4F \cdot \ln(10/0.21)$.
800 °C, the deviation might be due to the high impedance of the sample electrolyte. In the Zr-substituted samples, the measured EMFs are near to the theoretical value over the whole temperature range in comparison with the case of LaYO_3. This indicates that not only the based material of LaYO_3 but also the Zr-substituted oxide is conducted predominantly by ionic species, not by electrons. Figure 4 shows the current-voltage relation on discharging the above oxygen gas concentration cell using the x = 0.05 sample as an electrolyte. We can see that although the current is somewhat lower than that calculated using the bulk resistance by the ac impedance measurement, a steady electric current could be drawn from the cell. These results mean that the main charge carriers are oxide ions for the samples shown by LaY_{1-x}Zr_xO_{3+y/2}.

Thus we found oxide ion conduction in the substituted LaYO_3 phase. Considering the equation LaY_{1-x}Zr_xO_{3+y/2}, there should be excess oxide ions in the crystal. Here, several points should be borne in mind; considering the kind of the dopant cation, the high conductive phases such as stabilized zirconia (Y-SZ or La-SZ), or pyrochlore-type oxide (La_2Zr_2O_7) might be formed as a mixed phase, by which the conductivity increase would be ascribed. However, the corresponding XRD peak could not be observed even in the sample of x = 0.10, which we identified a mixed phasic oxide. Furthermore, it cannot be assumed that a few (< 0.025 mol%) coexistences of the conductive phase such as a stabilized zirconia caused considerably high oxide ionic conductivity, although we know that the highest oxide ion conductivity is 1.4 × 10^{-3} S cm^{-1} for the fully stabilized zirconia (cubic 8 mol% Y-SZ) at 1000 °C among the aforementioned oxide ion conductors, and it decreases down to 6.5 × 10^{-2} S cm^{-1} for the partially stabilized zirconia (tетragonal 3 mol% Y-SZ).22

We changed the substitution method from LaY_{1-x}Zr_xO_{3+y/2} to La_{1-x}Zr_xYO_{3+y/2}. In the latter case, almost the same experimental results were obtained as the former; the solid solution range extends up to x = 0.05, the sample of which showed fairly high oxide ion conductivity of 1.1 × 10^{-2} S cm^{-1} at 1000 °C (Fig. 5). If mixed phases were formed, the phasic and conductivity data would change depending on the coexistent phase, i.e., the kind of rare earth cations combined. The present results indicated that the zirconium cation can be substituted both for yttrium and lanthanum.

Nevertheless, we could not determine the exact positions of doped zirconium cations; especially zirconium cations might stay at the positions of nominal yttrium, and some yttrium cations move towards the lanthanum sites in the case of La_{1-x}Zr_xYO_{3+y/2}, although the zirconium positions could be inferred on the yttrium sites because of the cationic radii in the case of LaY_{1-x}Zr_xO_{3+y/2}. In any case, however, the substituted samples must have the excess oxide ions in the crystals. Thus, we measured the sample powder densities as to the samples of La_{1-x}Zr_xYO_{3+y/2} and compared them with those calculated using the lattice parameters measured by XRD and the assumption of the unit cell structures in two different models: [1] Oxygen interstitial lattice: La_{1-x}Zr_xYO_{3+y/2} as the doped zirconium atoms would ideally occupy some of the lanthanum sites and the excess interstitial oxide ions could be formed as was initially indicated in the nominal composition. [2] Cation vacancy lattice: La_{1-x}Zr_xY_{f}O_{1-f}, where f = 3/(3+x/2). If the number of oxide ions in the unit cell was strictly fixed, then some of the cation sites could be vacant. The valence change of metal ions cannot be considered in both cases. The results are indicated in Fig. 6. With increasing the zirconium content, the measured densities somewhat change, but not just on the line of case [1]; they are near to the

![Fig. 4 Current-voltage relation on discharging the oxygen gas concentration cell using the x = 0.05 sample as an electrolyte at 1000 °C. The cathode gas and anode gas were 1 atm oxygen and air, respectively. Dotted line shows the expected line calculated using Eo and the high frequency end on the real axis in the impedance plot.](image1)

![Fig. 5 Representative Arrhenius plots of conductivity measured in air for La_{2-x}Zr_xYO_{3+y/2}.](image2)
case [2] rather than the case [1]. However, we have to think of the following four points as to this result; (1) the difference between the cases [1] and [2] is very small in the present narrow solid solution range, (2) the density of the based material itself deviates from the theoretical one, (3) the absolute deviation of the observed from the theoretical is kept within 1.0% as same as the other powder density experiments (17) and (4) the composition dependence of the measured density is near to the case [1]. Then, the interstitial model in the case of [1] could be supported in total, which could probably explain the oxide ion conduction in pure LaYO$_3$ at high temperatures, but the case of [2] could not be completely refuted. In order to obtain the detailed conclusion, we must carry out a new analysis such as neutron diffraction, although it may be difficult to obtain the precise determination of ionic defects in the definitely narrow solid solution range. The results would furthermore lead to interesting elucidation of the ionic conduction via oxide ions.

We checked at least whether the perovskite-type LaYO$_3$ had a wide clearance in its ionic lattice; that is, its extra room not to be occupied by ions was compared with those of the perovskite of CaTiO$_3$ (23) the aforementioned scheelite-type oxide of PbWO$_4$ (24) and cubic 8 mol% yttria-stabilized zirconia (8YSZ) (25). Table 1 shows the lattice parameters, the ratios of occupied volume by ions (V$_2$) to the unit cell volume (V$_1$) and the resultant space ratio in each compound. The clearance ratio in LaYO$_3$ is fairly higher than those of CaTiO$_3$ and 8YSZ surprisingly, and is almost identical to that of PbWO$_4$, a based material of high oxide ion conductors. In these cases, the clearance ratios are the values simply calculated in the lattices and do not always correspond to the room in order to store excess oxide ions. However, we scientists know that there exists a fairly large clearance between the nearest lanthanum ions in a perovskite-type structure, which increases with larger ionic radii of two cations (La$^{3+}$ and Y$^{3+}$ in the present case). Considering furthermore that the ionic stacking and the resultant distortion of LaYO$_3$ is somewhat analogous to those of PbWO$_4$, oxide ion storage in the former lattice would be possible, which would bring about oxide ion conduction in the present substituted phase. Based on this idea, we are now going to investigate the other oxide systems that should include excess oxide ions and summarize their conduction and structure properties.

## 4 Conclusion

The perovskite-type oxide solid solutions were formed in the samples of ZrO$_2$-doped LaYO$_3$. The substituted samples showed fairly high oxide ion conduction as compared with the based material of LaYO$_3$. Zirconium substitution was possible in both the sites of lanthanum and yttrium, where the oxide ion conductivity increased with increasing zirconium content and, for example, the sample of x = 0.025 in La$_{1-x}$Zr$_x$O$_{3+x/2}$ had an oxide ion conductivity of $1.5 \times 10^{-2}$ S cm$^{-1}$ at 1000°C. Further zirconium substitution resulted in a mixed phase and a decrease of the conductivity. The oxide ion conduction in these perovskite-type phases was considered to be ascribed to interstitial oxide ion diffusion via excess oxide ions.

### Table 1: The ratios of occupied volume by ions (V$_2$) to the unit cell volume (V$_1$) and the resultant clearance ratios together with lattice parameters and ionic radii in the typical compounds.

<table>
<thead>
<tr>
<th>Compound (system)</th>
<th>Lattice parameter/Å</th>
<th>Cell vol. /Å$^3$</th>
<th>Ionic radius/Å Ion [CN]</th>
<th>Ionic vol. /Å$^3$</th>
<th>Clearance ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaYO$_3$ (orthorhombic)</td>
<td>$Z$</td>
<td>$a$</td>
<td>$b$</td>
<td>$c$</td>
<td>V$1$</td>
</tr>
<tr>
<td>8YSZ (cubic)</td>
<td>4</td>
<td>5.140</td>
<td>5.140</td>
<td>5.140</td>
<td>135.8</td>
</tr>
</tbody>
</table>

*1 extrapolated value from ionic radii at lower CN's.
References

25) SSCED-Web : http://riodb.ibase.aist.go.jp/ssced/