Doped $LaGaO_3$ Perovskite Type Oxide as a New Oxide Ionic Conductor

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Abstract: Doped $LaGaO_3$ exhibits high oxide ionic conductivity. Doping of Sr for the La site and Mg for the Ga site is the most effective method for enhancing the oxide ionic conductivity of $LaGaO_3$. The oxide ionic conductivity of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ was higher than that of Sc-doped ZrO_2 and slightly lower than that of Bi_2O_3 oxide. Furthermore, electronic or hole conduction was negligibly small in the oxygen partial pressure region from 1 to 10^{-20} atm.

Introduction

Oxide ion can migrate in an oxide lattice via oxide ion vacancies, and oxides in which electrical charges are mainly carried by oxide ions are called oxide ionic conductors. It is well-known that oxides with the fluorite structure, such as Y_2O_3-stabilized ZrO_2 (YSZ), exhibit excellent oxide ionic conduction at high temperature.[1] However, ionic conductivity of oxygen in oxides of other crystal structures has not yet been studied intensively. Perovskite type oxides, ABO_3, have stable crystal structures, and furthermore, a large number of oxide ion vacancies can be introduced into the lattice by the partial substitution of cation A or B with lower valence cations. However, migration of oxide ions in perovskite type oxides has yet to be studied thoroughly. Takahashi and Iwahara reported that the perovskite type oxide, $LaAlO_3$ doped with Ca, exhibits a high oxide ionic transference number over a wide range of oxygen partial pressure.[2] In our previous studies, oxide ionic conductivity of doped $NdAlO_3$ perovskite oxides was investigated and it was found that $Nd_{0.9}Ca_{0.1}AlO_3$ doped with Ga exhibited a comparable oxide ionic conductivity with that of Zr-based oxides with fluorite structure.[3] In this study, the oxide ionic conductivity of doped $LaGaO_3$ was investigated and it was found that the doped $LaGaO_3$ is a pure oxide ionic conductor with extremely high electrical conductivity over a wide range of oxygen partial pressure.

Experimental Section

Calculated amounts of commercial La_2O_3 (Wako, 99.99% pure), dopant oxide, and Ga_2O_3 (Kishida, 99.99% pure) were mixed for 3 h in a mortar with a pestle and then calcined at 1273 K for 6 h. The resulting powders were pulverized and pressed isostatically into a disk (20 mm diameter and 1 mm thickness) at 274.6 MPa in vacuo. The disks were sintered at 1773 K for 6 h unless otherwise noted. Platinum paste was applied on both faces of the disks as an electrode followed by firing at 1223 K for 10 min. The crystal structure of the specimens was measured with X-ray powder diffraction (Rigaku CN-2013) with the Cu $K\alpha$ line. The lattice parameter was calculated from several diffraction peaks in XRD in a wide range of diffraction angles, and then the lattice parameter of doped $LaGaO_3$ was estimated by extrapolation of the diffraction angle to 180° in a plot of the lattice parameter against the diffraction angle. The electrical conductivity of sintered samples (15 × 4 × 2 mm) was measured as a function of temperature (773–1273 K) and oxygen partial pressure (10^{-20}–1 atm) by the conventional dc four-probe method. When ion conductivity in solids is measured, the ac impedance method is better than the dc four-probe method; however, there was no difference between the electrical conductivity measured by the ac impedance method and the dc four-probe method. This is because the dc current for measurement

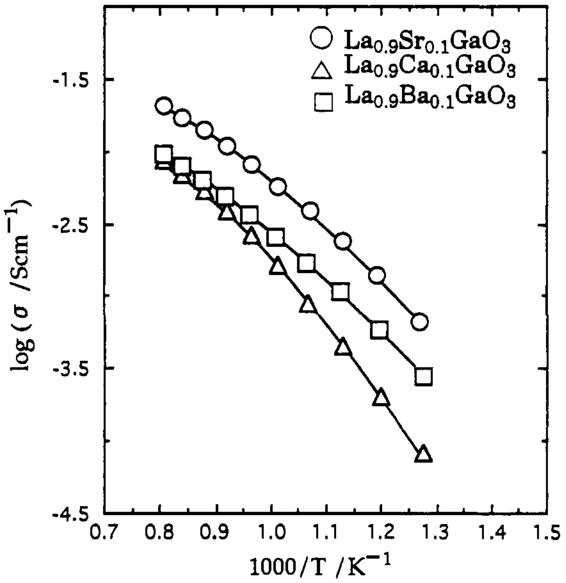

Figure 1. Effect of various alkaline earth cations doped for the La sites on the electrical conductivity of $La_{0.9}Mg_{0.1}GaO_3$ for M = Ca, Sr, Ba, ($P_{O2} = 10^{-5}$ atm).

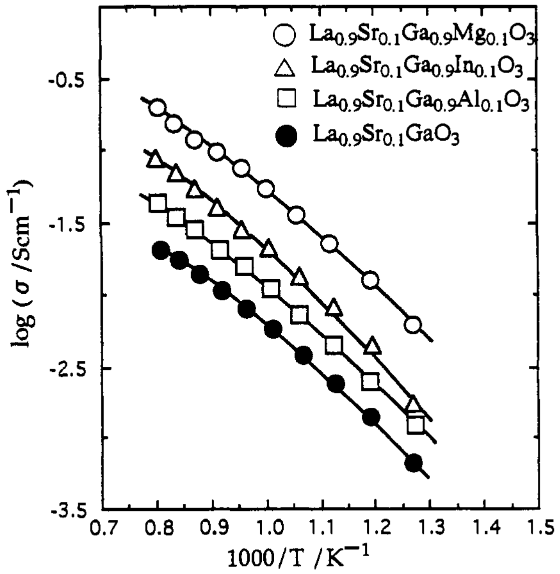

Figure 2. Effect of various cations doped for the Ga sites on the electrical conductivity of $La_{0.9}Sr_{0.1}Ga_{0.9}M_{0.1}O_3$ for M = Al, In, Mg ($P_{O2} = 10^{-5}$ atm).

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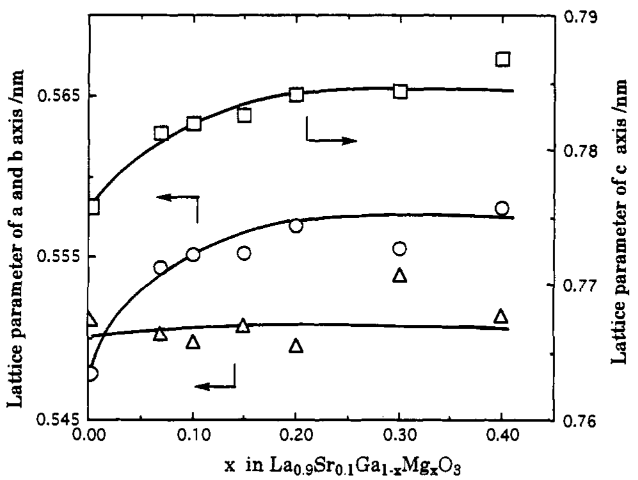

Figure 3. Lattice parameter of $La_{0.9}Sr_{0.1}Ga_{1-x}Mg_xO_3$ as a function of the x value. The lattice parameter was estimated by X-ray powder diffraction analysis with the Cu Kα line: (○) a axis, (△) b axis, (□) c axis.

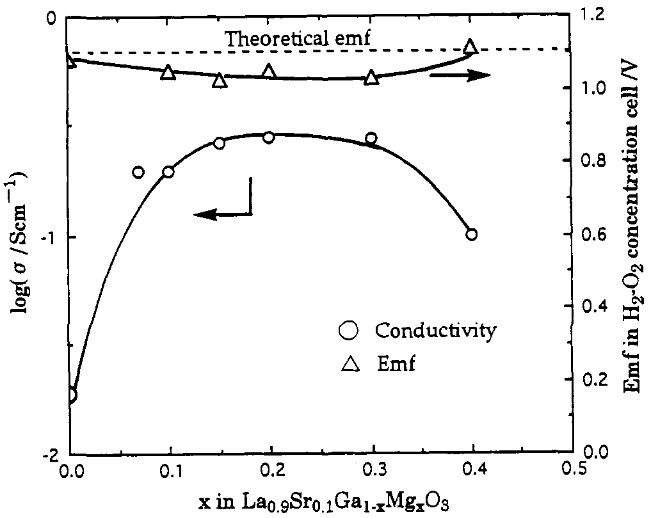

Figure 4. Effect of the amount of Mg substitution on the electrical conductivity of $La_{0.9}Sr_{0.1}Ga_{1-x}Mg_xO_3$ at 1223 K ($P_{O2} = 10^{-5}$ atm; the emf of an H_2–O_2 concentration cell with $La_{0.9}Sr_{0.1}Ga_{1-x}Mg_xO_3$ was used as the solid electrolyte at 1273 K).

is as small as a few milliamperes in this study. Furthermore, reproducibility of the measurement for oxide ionic conductivity was generally extremely high, less than 1%, provided that the sample is prepared by the same procedure under the same conditions (sintering temperature etc.). Accordingly, error bars for oxide ionic conductivity are emitted. The ionic transference number of oxygen, T_i, was estimated from the electromotive force (emf) of the oxygen concentration cell of H_2–O_2 at 873–1223 K.

Results and Discussion

Figure 1 shows the effects of alkaline earth cations added for the La sites in $LaGaO_3$ on the electrical conductivity. The electrical conductivity of $LaGaO_3$ depended strongly on the alkaline earth cations added for the La site and increased in the following order: Sr > Ba > Ca. The electrical conductivity increased with an increase in the amount of Sr additives and attained the maximum at $x = 0.1$ in $La_{1-x}Sr_xGaO_3$. Since the number of oxide vacancies increases with an increase in amount of Sr dopant, larger numbers of oxide vacancies are theoretically obtained and as a result higher oxide ion conductivity is consistent with larger amounts of Sr dopant. However, impure crystal phases such as $SrGaO_3$ and La_4SrO_7 were detected above $x = 0.1$ in $La_{1-x}Sr_xGaO_3$ by XRD analysis. Therefore, it is concluded that the limit of solid solution of Sr exists at about $x = 0.1$. The formation of second impure phases decreased the oxide ionic conductivity of specimens because the electrical conductivity of second phases such as $SrGaO_3$ or La_4SrO_7 is low. Consequently, the optimum amount of Sr addition for the La site seems to be $x = 0.1$ for increasing the oxide ionic conductivity of $LaGaO_3$.

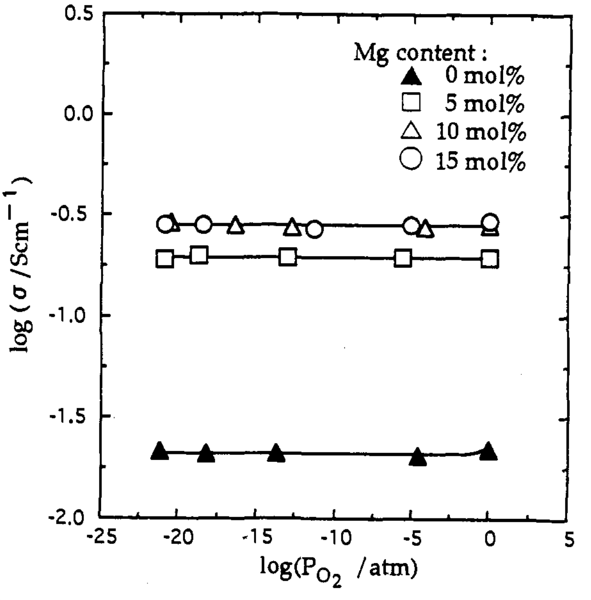

Figure 5. Electrical conductivity of $La_{0.9}Sr_{0.1}Ga_{1-x}Mg_xO_3$ at 1123 K as a function of oxygen partial pressure.

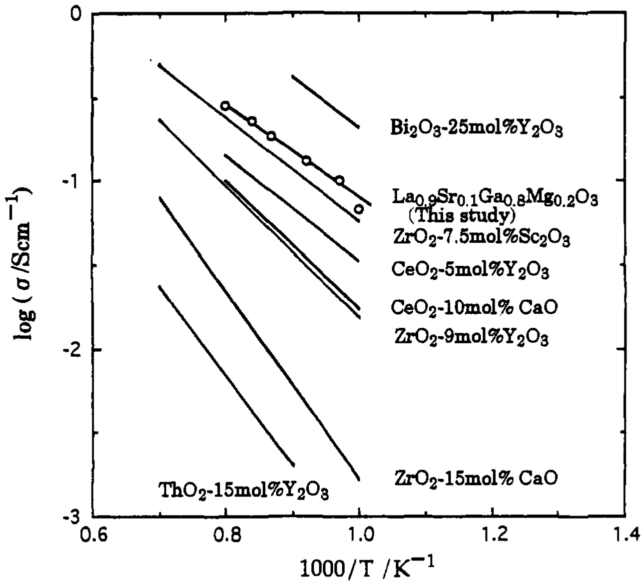

Figure 6. Comparison of the oxide ionic conductivity of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ with conventional oxide ion conductors with fluorite structures. The conductivity of the conventional ionic conductor with fluorite structure was cited from ref 6.

The effects of additives at the Ga site of $La_{0.9}Sr_{0.1}GaO_3$ on the electrical conductivity were also studied to further enhance the electrical conductivity as shown in Figure 2. Electrical conductivity was improved by doping with Mg, Al, or In for the Ga site in $LaGaO_3$. In particular, addition of Mg was the most effective method for increasing the electrical conductivity among the dopants examined.

The crystal structure of undoped and doped $LaGaO_3$ is orthorhombic at room temperature.[4] Figure 3 shows the lattice parameter of Mg-doped $La_{0.9}Sr_{0.1}GaO_3$ estimated by X-ray powder diffraction pattern. The ionic radius of Mg^{2+} is 0.086

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(4) Wang, Y.; Liu, X.; Yao, G. D.; Liebermann, R. C.; Dudley, M. *Mater. Sci. Eng.* **1991**, *A132*, 13.

nm which is larger than that of Ga^{3+} (0.076 nm) but smaller than that of La^{3+} (0.130 nm).[5] Since no impure crystal phases were detected by XRD analysis and the lattice parameters were increased with increases in the amount of Mg content as shown in Figure 3, all of the added Mg seems to have solved substitutionally into the Ga site of $LaGaO_3$. Although the second crystal phases could not be recognized by XRD analysis up to $x = 0.4$, the limit of solid solution of Mg for the Ga site seems to exist at about $x = 0.2$, since the lattice parameter was independent of Mg content above $x = 0.2$.

The electrical conductivity at 1223 K and the transference number determined with an H_2–O_2 concentration cell at 1273 K are shown in Figure 4 as a function of the number of Mg additives for the Ga site in $LaGaO_3$. The electrical conductivity increased with increasing Mg content and was a maximum at $x = 0.2$ in $La_{0.9}Sr_{0.1}Ga_{1-x}Mg_xO_3$. Since the limit of solid solution of Mg for the Ga site exists at about $x = 0.2$, the oxide ionic conductivity seems to be the maximum at $x = 0.2$. Figure 5 shows the electrical conductivity of $La_{0.9}Sr_{0.1}Ga_{1-x}Mg_xO_3$ at 1223 K as a function of the oxygen partial pressure. The electrical conductivity of these specimens was almost independent of the oxygen partial pressure in the range from $P_{O2} = 10^{-20}$ to 1 atm at 1223 K. On the other hand, an almost theoretical emf was obtained upon the H_2–O_2 oxygen gas concentration cell where $La_{0.9}Sr_{0.2}Ga_{1-x}Mg_xO_3$ was applied for the electrolyte as shown in Figure 4. This suggests that the perovskite oxide of Mg-doped $La_{0.9}Sr_{0.1}Ga_{1-x}Mg_xO_3$ is almost a pure oxide ionic conductor over a wide range of oxygen partial pressures.

The oxide ionic conductivity of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ is shown in Figure 6 with those of the conventional oxide ionic conductors.[6] Oxide ionic conductivity of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ is higher than the typical conductivities of ZrO_2- or CeO_2-based oxides and somewhat lower than those of Bi_2O_3-based oxides. It is well-known that n-type semiconduction is dominant in CeO_2- or Bi_2O_3-based oxides under a low oxygen partial pressure,[7,8] and furthermore, thermal stability is not satisfactory in Bi_2O_3-based oxides. In contrast, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ exhibited only oxide ion conductivity from $P_{O2} = 10^{-20}$ to 1 atm. It can be concluded that $LaGaO_3$ doped with Sr and Mg is a promising new oxide ionic conductor.

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