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Proton transport properties of $La_{0.9}M_{0.1}YbO_{3-\delta}$ (M = Ba, Sr, Ca, Mg)

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ABSTRACT

The proton transport properties of $La_{0.9}M_{0.1}YbO_{3-\delta}$ (M = Ba, Sr, Ca, Mg) were studied by the electrical conductivity measurement technique in the temperature range of 673–1173 K. The proton concentration was estimated by the weight changes due to the hydration reaction. The electrical conductivity and proton concentration of $La_{0.9}Ba_{0.1}YbO_{3-\delta}$ were the highest in $La_{0.9}M_{0.1}YbO_{3-\delta}$. The electromotive force of a hydrogen gas concentration cell using $La_{0.9}Ba_{0.1}YbO_{3-\delta}$ as the electrolyte was observed at 673–1073 K, and was in a good agreement with the theoretical values assuming that the proton transport number was unity.

1. Introduction

Some oxides with the perovskite structure, $A^{3+}B^{3+}O_3$, show protonic conduction [1–6], and have been attracting attention as key materials for electrochemical devices, such as chemical sensors [7–10], fuel cells [11,12], and steam electrolysis cells [13]. In the 1980s, Takahashi and Iwahara reported that $LaYO_3$ doped with Ca exhibited a proton conductivity [1]. Since then, the proton transport properties of many La-based perovskites, e.g., $La_{0.9}Sr_{0.1}YO_{3-\delta}$ [14], $La_{0.9}M_{0.1}ErO_{3-\delta}$ (M = Ca, Sr, Ba) [15], $La_{0.9}Sr_{0.1}Sc_{0.9}Mg_{0.1}O_3$ [16], $La_{0.9}Sr_{0.1}MO_3$ (M = Sc, In and Lu) [17] and $La_{1-x}Sr_xScO_{3-\delta}$ [18], have been clarified in detail. The results of these studies suggest that the conductivity of $La_{0.9}Sr_{0.1}MO_3$ (M = Sc, In, Lu, Er, Y) has a tendency to increase with the decrease in the ionic radii of the B site ions.

$LaYbO_3$ has a perovskite structure and is a potential material as proton conducting oxide with a good chemical stability. The conductivities of undoped $LaYbO_3$ and $La_{0.95}Ca_{0.05}YbO_{3-\delta}$ have been reported by Strelkov et al. [19], Dubok et al. [20] and Feteira et al. [21]. However, the conduction mechanism and effect of dopants were not described in these papers. For the effective use of $LaYbO_3$ as a solid electrolyte, it is important to understand the effect of dopants on the conductivity, the concentration of defects, ionic transport number, etc. The purpose of this study is to examine the electrical properties of various $La_{0.9}M_{0.1}YbO_{3-\delta}$ (M = Ba, Sr, Ca, Mg) materials.

2. Experimental

2.1. Sample preparation

Samples $La_{0.9}M_{0.1}YbO_{3-\delta}$ (M = Ba, Sr, Ca, Mg) and undoped $LaYbO_3$ were prepared by a solid-state reaction method. The reagent-grade La_2O_3 (99.9%), Yb_2O_3 (99.9%), $BaCO_3$ (99.9%), $SrCO_3$ (99.9%), $CaCO_3$ (99.9%) and MgO (99.9%) powders were weighted to form the composition $La_{0.9}M_{0.1}YbO_{3-\delta}$ (M = Ba, Sr, Ca, Mg), then mixed in ethanol using mortar. The powder mixtures were annealed for 10 h in air at 1673 K. The annealed powder was mixed using a ball mill and pressed into pellets at 300 MPa. The pellets were then sintered at 1973 K for 10 h in air. We used samples with a compact density of 95% or higher for the measurements. X-ray powder diffraction analysis (XRD) of the samples gave well-defined perovskite patterns (orthorhombic). $La_{0.9}Ca_{0.1}YbO_{3-\delta}$ contained CaO as a secondary phase. The other samples were confirmed to be a single phase of perovskite. The lattice constants were shown in Table 1.

2.2. Measurement of electrical conductivity

The electrical conductivity was measured under $1.9\%H_2O$–$1\%H_2$–Ar by a four-probe AC technique. The complex impedance was measured in the frequency range 0.1 Hz–1 MHz

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Table 1
The lattice constants of $La_{0.9}M_{0.1}YbO_{3-\delta}$.

Dopant species (*M*)	*a* (nm)	*b* (nm)	*c* (nm)
Ba	0.6023	0.5831	0.8413
Sr	0.6026	0.5844	0.8407
Ca	0.6023	0.5825	0.8402
Mg	0.6021	0.5820	0.8398

using an impedance analyzer (VerasSTAT 3). Porous platinum electrodes were prepared on each end of the bar sample (10.0 mm × 3.0 mm × 2.0 mm) by a painting paste and then sintering at 1273 K in air. In order to verify the protonic conductivity, the electrical conductivity was measured under 1.9%H_2O–O_2 and 1.9%D_2O–O_2 in the temperature range of 573–1173 K.

2.3. Measurement of the electromotive force of gas concentration cell

The EMF of the gas concentration cells was measured for $La_{0.9}Ba_{0.1}YbO_{3-\delta}$ in temperature range of 673–1073 K. The samples were formed into pellets shape (φ13.5 mm diameter and 0.5 mm thickness). Porous platinum electrodes were prepared on both surfaces of the pellet samples. The samples were held between the alumina tubes with pyrex glass gaskets, separating two electrode compartments. The gas concentration cell is represented by the following cell formula:

$$(-), \mathrm{Pt}(p_{H_2(I)}, p_{H_2O(I)}) \left| La_{0.9}Ba_{0.1}YbO_{3-\delta} \right| \mathrm{Pt}(p_{H_2(II)}, p_{H_2O(II)}), (+) \quad (1)$$

where p_i in this paper represents the activities of the gas species with reference to one bar of the respective gas in the pure state. A gas mixture of H_2 and Ar was humidified with water vapor saturated at a given temperature using a bubbler in a thermostatic bath.

The EMF measurements were performed using an electrometer (HE-104, Hokuto Denko).

2.4. Measurement of the proton concentrations

The proton concentrations of $La_{0.9}M_{0.1}YbO_3$ (*M* = Ba, Sr, Ca, Mg) and undoped $LaYbO_3$ were determined in the temperature range of 558–1473 K by a thermogravimetric analysis (TGA). The TGA was performed for both the powder (grain size: 5–20 μm) and bar (10.0 mm × 3.0 mm × 2.0 mm) samples using a STA449F3 Jupiter NETZSCH. The samples were first heated at 1473 K for one hour under dry-10%O_2–Ar to remove the hydrogen. The weight changes were then measured in 1.9% H_2O–10% O_2–Ar in the temperature range of 558–1473 K. In order to eliminate the buoyancy effect, the measured weight change was corrected for the result of blank test without sample.

3. Results

3.1. Electrical conductivity of $La_{0.9}M_{0.1}YbO_{3-\delta}$ (*M* = Ba, Sr, Ca, Mg)

The electrical conductivity of $La_{0.9}Sr_{0.1}YbO_{3-\delta}$ equilibrated with 1.9% H_2O–O_2 and 1.9% D_2O–O_2 is shown as a function of the temperature in Fig. 1. The H^+/D^+ isotope effect on the conductivity was observed in the temperature range of 573–873 K. However, the ratio of the total conductivity in H_2O to D_2O decreased with an increase in the temperature, which leads to a decreased proton transport number with the increasing temperature.

The effect of the dopant on the conductivity is shown in Fig. 2. The conductivity of $La_{0.9}Ba_{0.1}YbO_{3-\delta}$ was the highest of all the $La_{0.9}M_{0.1}YbO_{3-\delta}$ studied. The conductivity increased in the order of Mg, Ca, Sr, Ba. In comparison with the conductivity of $La_{0.9}Sr_{0.1}RO_{3-\delta}$ (*R* = Sc, In, Lu, Er, Y), the conductivity of $La_{0.9}Sr_{0.1}YbO_{3-\delta}$ was slightly lower than that of $La_{0.9}Sr_{0.1}YO_{3-\delta}$ and $La_{0.9}Sr_{0.1}LuO_{3-\delta}$.

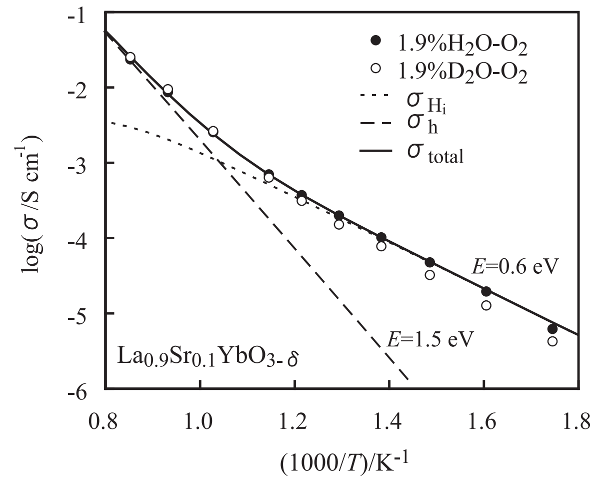

Fig. 1. H+/D+ isotope effect on the electrical conductivity for $La_{0.9}Sr_{0.1}YbO_{3-\delta}$.

Fig. 3(a) shows the dependence of the electrical conductivity of $La_{0.9}Ba_{0.1}YbO_{3-\delta}$ on the water vapor activity in the reducing atmosphere containing hydrogen. The conductivity was independent of the water vapor activities at 873 K. On the other hand, the conductivity was slightly dependant on the water vapor activity at 1173 K.

Fig. 3(b) shows the oxygen activity dependence of the conductivity at a fixed water vapor activity ($p_{H_2O} = 0.019$). The conductivity was independent of the oxygen activity under the H_2O/H_2. On the other hand, the conductivity was found to be proportional to the one-quarter power of the oxygen activity under the H_2O/O_2 at 1173 K.

3.2. The electromotive force of gas concentration cell using $La_{0.9}Ba_{0.1}YbO_{3-\delta}$

The EMF of the gas concentration cell was measured for $La_{0.9}Ba_{0.1}YbO_{3-\delta}$ in a hydrogen atmosphere to determine the charge carriers. Fig. 4(a) shows the EMF of the hydrogen

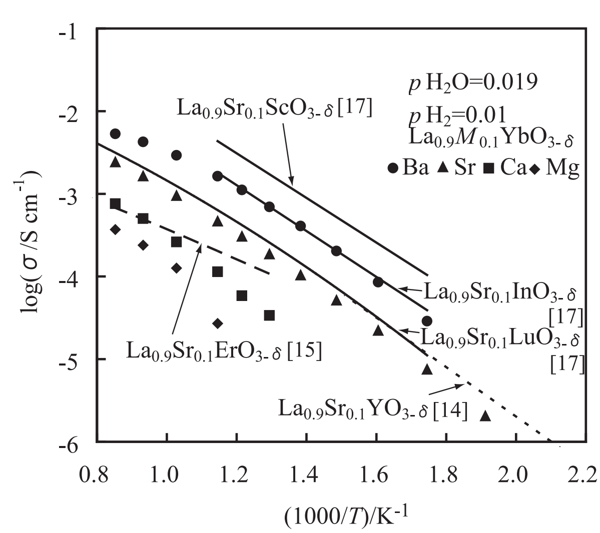

Fig. 2. The effect of dopant species on the electrical conductivity.