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Short Note

Protonic Conduction in the Single Crystals of $SrZr_{0.95}M_{0.05}O_3$ (M = Y, Sc, Yb, Er)

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The protonic conductivities of $SrZr_{0.95}M_{0.05}O_3$ doped with four acceptor ions ($M^{3+} = Y^{3+}, Sc^{3+}, Yb^{3+}, Er^{3+}$) have been studied in the single crystal form. The protonic conductivity is found in four acceptor ions, indicating that protons migrate by hopping from site to site. The Yb-doped crystal has the lowest activation energy and the highest conductivity amongst the four acceptor ions. This is considered to be due to the difference in strength of the O–H bond with different acceptor doping.

KEYWORDS: protonic conductivity, $SrZrO_3$, acceptor, O–H bond, activation energy

Strontium zirconate ($SrZrO_3$) shows protonic conductivity at high temperature when acceptor ions are doped in the Zr ion site.[1–3] Such an oxide-type protonic conductor is a type of solid electrolyte in which the protons can migrate. Protonic conductivity at high temperature has many promising potential electrochemical applications such as in hydrogen sensors or fuel cells. It is known that Y-doped $SrZrO_3$ ($SrZr_{1-x}Y_xO_3$) is a good protonic conductor which can be used in relatively high temperature regions.[2,3] The protonic conductivity is referred to as hole conduction; the proton transfer numbers decrease at high temperatures above 700°C. Infrared absorption (IR) and neutron diffraction studies[3–6] indicate that the protons form hydrogen bonds between two oxygen ions and migrate by a thermal activation process. However, the conductivity depends on the concentration of Y^{3+} ions. When Y^{3+} ions are doped with 4 mol% ($x = 0.04$), the conductivities are higher than the other crystals.

In the present study, the electrical conductivity of $SrZrO_3$ doped with one of four acceptor ions (Y^{3+}, Sc^{3+}, Yb^{3+} and Er^{3+}) was measured in the temperature region of 80 to 900°C under dry air and H_2O atmosphere. We discuss how the proton conductivity is related to the ionic radius of the acceptor.

The sample was prepared by the solid-state reaction of $SrZrO_3$, $SrCO_3$, and M_2O_3 (M = Y, Sc, Yb, Er) at 1200°C for about 12 h, and the single crystals were grown by a floating zone method using a Xe-arc imaging furnace. The single crystals were grown in an atmosphere of oxygen to prevent protons from entering the crystal. The prepared crystals were transparent and shaped in a rectangular column of about $1.5 \times 0.8 \times 8\,mm^3$. The M^{3+} ion is clearly to be doped as an acceptor ion in the Zr^{4+} ion site of $SrZrO_3$ as observed by a simple thermoelectromotive force experiment. The dopant concentration is 5 mol%. The single crystals were confirmed as being in a single phase with a perovskite structure by powder X-ray diffraction analysis. The crystals were placed in an atmosphere of saturated water vapor pressure at 19°C. In the case of dry air, a cooling trap of liquid N_2 was used to prevent protons from entering the crystals.

The complex impedance was measured using a HP4275A LCR meter, which covers the frequency range from 10 kHz to 10 MHz. The bulk impedance plot is obtained without the interfacial impedance by plotting a semicircle as shown in Fig 1. The intersection of the semicircle with the real axis gives the bulk impedance of the specimen. The complex impedance was also measured for other acceptor ions and similar results were obtained.

Figure 2(a) shows the isotope effect of the conductivities of $SrZr_{0.95}Y_{0.05}O_3$ measured in an atmosphere of saturated H_2O vapor or D_2O vapor at 19°C. The conductivity of the specimen was also measured in dry air. The conductivity in

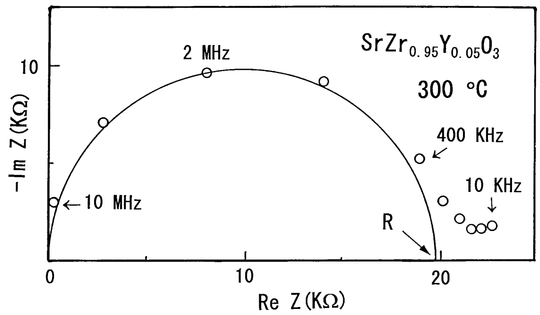

Fig. 1. Complex impedance plot of $SrZr_{0.95}Y_{0.05}O_3$ measured at 300°C.

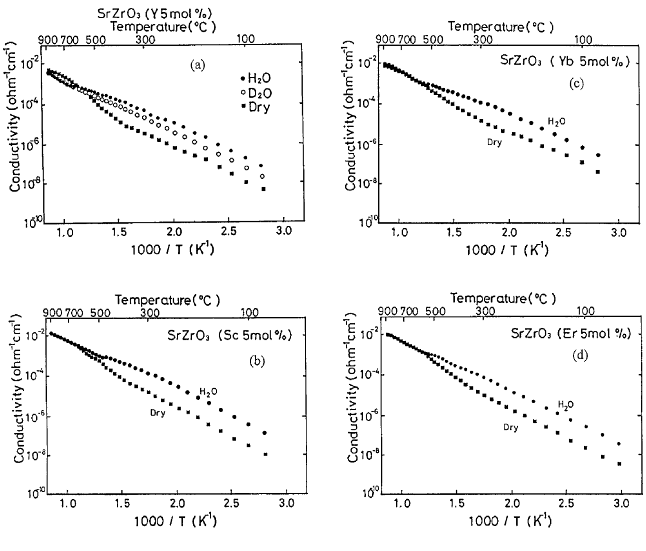

Fig. 2. Arrhenius plot of the electrical conductivities in (a) $SrZr_{0.95}Y_{0.05}O_3$, (b) $SrZr_{0.95}Sc_{0.05}O_3$, (c) $SrZr_{0.95}Er_{0.05}O_3$ and (d) $SrZr_{0.95}Er_{0.05}O_3$. Solid circle, open circle, and squares indicate H_2O, D_2O, and dry air atmospheres.

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D_2O vapor is always lower than that in H_2O vapor and higher than that in dry air, indicating that protons migrate by hopping from site to site. Figures 2(b)–2(d) show the results of the conductivities of $SrZr_{0.95}Sc_{0.05}O_3$, $SrZr_{0.95}Er_{0.05}O_3$ and $SrZr_{0.95}Er_{0.05}O_3$, respectively. These conductivities show thermal activation-type behavior at high-temperature regions of 80 to 900°C. In the temperature region of 300 to 600°C, the conductivities in H_2O vapor become larger than those in dry air. The main carriers are holes in dry atmosphere and protons in H_2O atmosphere below 600°C. Above 600°C, the conductivities are almost the same in both dry and H_2O atmospheres, indicating that the carriers are holes or oxygen vacancies rather than protons or deutrons. Similar features are observed for other perovskite-type protonic conductors. The transition temperature from the hole to the proton is much lower than that of Y-doped $SrCeO_3$ and higher than that of Sc-doped $SrTiO_3$.[3,4] However, the transition temperature of $SrZrO_3$ does not depend on the ionic radius of the acceptor.

Figure 3(a) shows the conductivities at 100°C shown in Fig. 2 vs the ionic radius of the acceptor. Except for Yb^{3+} ions, the conductivity decreases with increasing ionic radius. Furthermore, the activation energy estimated from the slope of the Arrhenius plot decreases with increasing ionic radius, as shown in Fig. 3(b). The protonic conduction depends on the ionic radius of the acceptor. Recently, Yugami *et al.*[7] studied the acceptor ion dependence of $SrZr_{0.95}M_{0.05}O_3$ using IR spectra of OH-stretching. Four absorption bands, which correspond to four different sites of protons, are observed in the wave number range from 2000 to 3500 cm^{-1}. The absorption band of the high-energy side ($\sim 3200\,cm^{-1}$), which is assigned to the proton site accompanying a dopant cation, significantly decreases with increasing ionic radius of the acceptor, although the other three absorption bands do not change. On the other hand, it has been reported that the distance between two oxygen ions decreases and the strength of the O–H bond decreases due to the hydrogen-bond effect when the ionic radius of the doped acceptor is larger than that of the host lattice.[8] The ionic radius of Sc^{3+} is close to that of Zr^{4+} (0.072 nm). It is considered that this relatively small difference between Sc^{3+} and Zr^{4+} compared to the large size difference between Zr^{4+} and other acceptor ions contributes to the high population of protons.

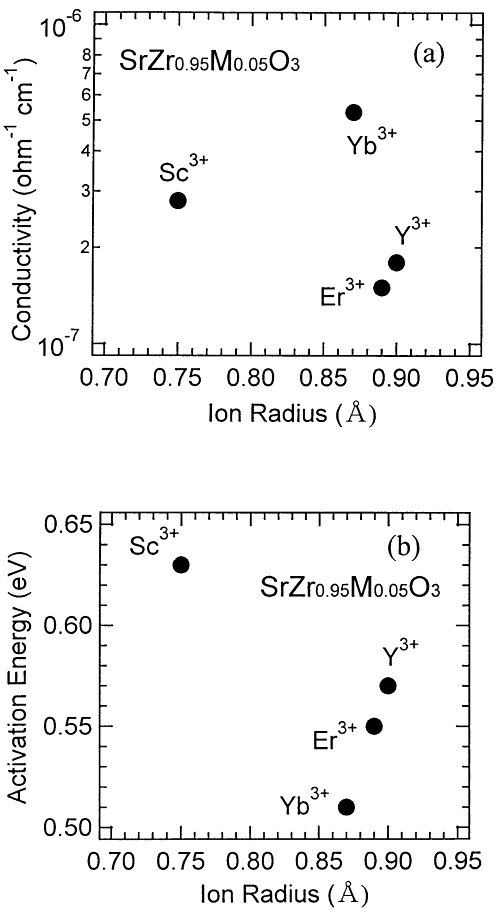

Fig. 3. Electrical conductivity at 100°C and (b) activation energy plotted against the ionic radius of the acceptor.

In recent years, the concentrations of protons, holes, and oxide ion vacancies in protonic conductor In-doped $CaZrO_3$ have been estimated from the defect chemical analysis.[9–11] The holes and oxygen vacancies created by In^{3+} doping decrease by proton doping, indicating that the doped proton is exchanged with the hole and oxygen vacancy in the crystal lattice. This fact is supported by the results of photoemission study.[11] However, the holes and oxygen vacancies of $SrZr_{0.95}M_{0.05}O_3$ do not depend on the ionic radius of the acceptor since the crystals used in this study were confirmed to be electroneutral condition. The above results indicate the difference in the concentration of protons due to the ionic radius of the acceptor which corresponds to the change in the absorption band of the high-energy side ($\sim 3200\,cm^{-1}$) observed in the IR spectra.[7]

In conclusion, it has been determined that the protonic conduction of $SrZrO_3$ is found in four acceptor ions (Y^{3+}, Sc^{3+}, Yb^{3+} and Er^{3+}). The activation energy decreases with the increasing ionic radius of the acceptor. This is considered to be due to the difference of the O–H bond length depending on the ionic radius of the acceptor.

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1) H. Iwahara, T. Esaka, H. Uchida and N. Maeda: Solid State Ionics **3–4** (1980) 359.
2) H. H. Huang, M. Ishigame and S. Shin: Solid State Ionics **47** (1991) 251.
3) S. Shin, H. H. Huang, M. Ishigame and H. Iwahara: Solid State Ionics **40/41** (1990) 910.
4) N. Sata, K. Hiramoto, M. Ishigame, S. Hosoya, N. Niimura and S. Shin: Phys. Rev. B **54** (1996) 15795.
5) N. Sata, S. Shin, K. Shibata and M. Ishigame: J. Phys. Soc. Jpn. **68** (1999) 3600.
6) O. Kamishima, T. Hattori, K. Ohota, Y. Chiba and M. Ishigame: J. Phys. Condens. Matter **11** (1999) 5355.
7) H. Yugami, Y. Shibayama, S. Matsuo, M. Ishigame and S. Shin: Solid State Ionics **85** (1996) 319.
8) A. Novac: Struct. & Bond. **18** (1974) 177.
9) S. Yamaguchi, K. Kobayashi, T. Higuchi, S. Shin and Y. Iguchi: Solid State Ionics **136–137** (2000) 305.
10) K. Kobayashi, S. Yamaguchi and Y. Iguchi: Solid State Ionics **108** (1998) 355.
11) T. Higuchi, T. Tsukamoto, Y. Tezuka, K. Kobayashi, S. Yamaguchi and S. Shin: Jpn. J. Appl. Phys. **39** (2000) L 133.