Short Note

Protonic Conduction in the Single Crystal of $SrTi_{1-x}Sc_xO_3$

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The proton conduction of Sc-doped $SrTiO_3$ ($SrTi_{1-x}Sc_xO_3$) has been studied in the single crystal form. The $SrTi_{1-x}Sc_xO_3$ crystals exhibit significantly higher conductivities than the pure ones, and the crystal with $x = 0.02$ exhibits sufficiently higher conductivity than any other. The activation energy of $SrTi_{1-x}Sc_xO_3$ crystals decreases rapidly with increasing Sc^{3+} concentration at $x \leq 0.02$, then increases slightly when $x \geq 0.02$. These results indicate that the protonic conduction of $SrTi_{1-x}Sc_xO_3$ depends on the Sc^{3+} dopant concentration. [DOI: 10.1143/JJAP.41.2120]

KEYWORDS: proton conductivity, $SrTi_{1-x}Sc_xO_3$, hole, activation energy, electronic structure

The perovskite-type oxides of general formula ABO_3 have been receiving considerable attention as a solid-state proton conductor for a wide range of promising electrochemical applications such as fuel cells, gas sensors, and hydrogen pumps.[1–5] Most of the attention has been focused on cerates and zirconates because of their excellent proton conductivity and chemical stability. Their transport and structural properties have been extensively studied by Shin's group[2–6] and Yamaguchi's group.[7–11] Furthermore, theoretical investigations of the mechanism of proton migration have also been reported in perovskite-type oxides.[12–17] The main charge carrier can be a proton, oxygen ion or hole, and the dominant conductivity region depends on the value of oxygen vacancy or hydrogen fugacity. The amount of the main charge carrier also depends on the proton conductivity. For Y-doped $SrZrO_3$ ($SrZr_{1-x}Y_xO_3$), the proton conductivity is referred to as hole conductivity; the rate of proton transfer decreases at high temperatures above 700°C. The proton conductivity increases significantly with the concentration of Y^{3+} ions and becomes almost constant at $x \geq 0.05$.[2,3]

Sata *et al.* reported that $SrTiO_3$ also shows proton conductivity with a very low activation energy when Sc^{3+} ions are doped with 4 mol% ($SrTi_{0.96}Sc_{0.04}O_3$).[4] The electrical conductivity exhibits a thermal-activation-type behavior with an activation energy (E_A) of about 0.4 eV, suggesting that protons migrate by hopping from site to site around the oxygen ion in this material. Neutron diffraction and infrared absorption studies indicate that protons are located on the side opposite the Ti^{4+} (or Sc^{3+}) ion with respect to a line connecting the two oxygen ions[4] and migrate by a thermal activation process. Furthermore, the potential barrier for local protonic motion in $SrTi_{0.95}Sc_{0.05}O_3$ has been studied by hole burning spectroscopy. It was reported that the potential barrier is 2 times lower than the activation energy obtained from the electrical conductivity measurements. However, the Sc^{3+} dopant dependence for proton conduction in $SrTiO_3$ has not been reported thus far.

In this study, the Sc^{3+} concentration dependence of the electrical conductivity of Sc-doped $SrTiO_3$ ($SrTi_{1-x}Sc_xO_3$) was measured in the temperature region of 30 to 900°C in H_2O atmosphere. We report in this paper that the proton conduction of $SrTi_{1-x}Sc_xO_3$ depends on the concentration of Sc^{3+} ions, as shown in $SrZr_{1-x}Y_xO_3$.[2,3]

The $SrTi_{1-x}Sc_xO_3$ samples were prepared by the solid-state reaction of $SrTiO_3$, $SrCO_3$, and Sc_2O_3 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 O_2 atmosphere to prevent the 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 Sc^{3+} ion was found to be doped as an acceptor ion in the Ti^{4+} ion site of $SrTiO_3$ by a simple thermoelectromotive force experiment. The single crystals were confirmed to be a single phase with perovskite structure by powder X-ray diffraction analysis. The crystals were kept in an atmosphere of saturated H_2O vapor pressure at 20°C. Electrical conductivity measurements were performed using an LCR meter (HP4275A) with a frequency range from 10 kHz to 10 MHz.

Figure 1 shows the Arrhenius plots as a function of Sc^{3+} ions of proton-doped $SrTi_{1-x}Sc_xO_3$ measured in the atmosphere of saturated H_2O vapor at 20°C. It is clear that the conductivity of $x = 0$ is different from that in the case of Sc^{3+} ions. These conductivities show thermal-activation-type behavior in the temperature region of 30 to 900°C. The conductivities increase significantly with increasing Sc^{3+} dopant concentration at $x \leq 0.02$, then decrease slightly when $x > 0.02$. The Arrhenius plots are divided into three
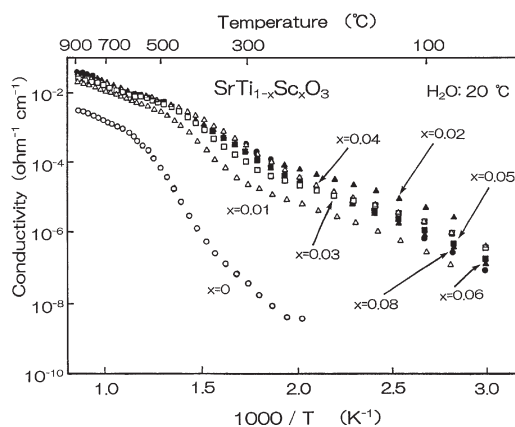
Fig. 1. Arrhenius plot of the electrical conductivity as a function of Sc^{3+} doping of proton-doped $SrTi_{1-x}Sc_xO_3$ measured in atmosphere of saturated H_2O vapor at 20°C.

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regions, namely, a high-temperature region above ∼450°C, an intermediate temperature region between ∼300 and ∼450°C, and a low-temperature region below ∼300°C. Each temperature region has a different slope, which is attributed to the difference in the activation energy. Since the hole and oxygen ion conductions are dominant at high temperatures, and proton conduction is dominant at low temperatures, it is considered that the main carriers are protons below ∼300°C, and holes or oxygen vacancies, rather than protons, above ∼450°C. The intermediate temperature region is considered to be the saturation region, in which the change from proton conduction to hole conduction occurs. This result corresponds to the result of $SrTi_{0.96}Sc_{0.04}O_3$.[4]

Figure 2(a) shows the electrical conductivity measured at about 100°C shown in Fig. 1 vs Sc^{3+} dopant concentration (mol%). The conductivity increases significantly with increasing Sc^{3+} dopant concentration at $x < 0.02$, but decreases slightly at $x \geq 0.02$. Sc^{3+} ions produce holes and protons, leading to the increase of the conductivity at $x \leq 0.02$; however, highly doped crystals structures could be somewhat distorted, leading to the decrease of the conductivity at $x \geq 0.02$. The doped crystals exhibit sufficiently higher conductivities than the pure ones, and the crystal with $x = 0.02$ exhibits higher conductivity than any other.

Figure 2(b) shows E_A, estimated from the slope of the Arrhenius plot, vs Sc^{3+} dopant concentration (mol%). As a reference, the E_A of dried $SrTi_{1-x}Sc_xO_3$ obtained from ref. 18 is also shown in this figure. The E_A of proton-doped $SrTi_{1-x}Sc_xO_3$ is usually lower than that of dried $SrTi_{1-x}Sc_xO_3$. In proton-doped $SrTi_{1-x}Sc_xO_3$, E_A decreases significantly from 0.42 to 0.36 eV at $x \leq 0.02$ and increases from 0.36 to 0.56 eV at $x \geq 0.02$. In dried $SrTi_{1-x}Sc_xO_3$, E_A decreases rapidly from 0.77 to 0.63 eV at $x \leq 0.02$ and increases from 0.63 to 0.77 eV at $x \geq 0.02$. The crystal with $x = 0.02$ exhibits lower E_A than any other. The above results indicate that the proton or the hole conduction depends on the Sc^{3+} dopant concentration.

In recent years, the electronic structure of proton conductor $SrTi_{1-x}Sc_xO_3$ has been studied using X-ray absorption spectroscopy (XAS).[18,19] In dried $SrTi_{1-x}Sc_xO_3$, the XAS spectra below the O $1s$ threshold show two empty features whose energy positions match with the hole state at the top of the valence band and the acceptor level above the Fermi level (E_F). However, the hole state and the acceptor level decrease due to proton doping. Furthermore, a new structure is found at a level below E_F, which is considered to be the proton-induced level. These findings indicate that the doped protons replaced the holes and oxygen vacancies in the crystal lattice. Therefore, the charge of $SrTi_{1-x}Sc_xO_3$ at temperatures below 300°C is compensated by the protons created at the hole state of the top of the valence band. In contrast, the ionic crystal forms a polaron, which brings about lattice distortion by doping. The hole in $SrTi_{1-x}Sc_xO_3$ is expected to migrate as a small polaron that exists in the oxygen ions.

In conclusion, we studied the proton conduction in single crystals of $SrTi_{1-x}Sc_xO_3$. The electrical conductivity is related to the hole or oxygen ion conduction at temperatures above 300°C and to the proton conduction below 300°C. The doped crystals exhibit sufficiently higher conductivities than the pure ones, and the crystal with $x = 0.02$ exhibits higher conductivity than any other. E_A decreases rapidly with increasing Sc^{3+} concentration at $x \leq 0.02$, then decreases slightly when $x \geq 0.02$. It is concluded that the proton conduction of $SrTi_{1-x}Sc_xO_3$ depends on the Sc^{3+} dopant concentration.
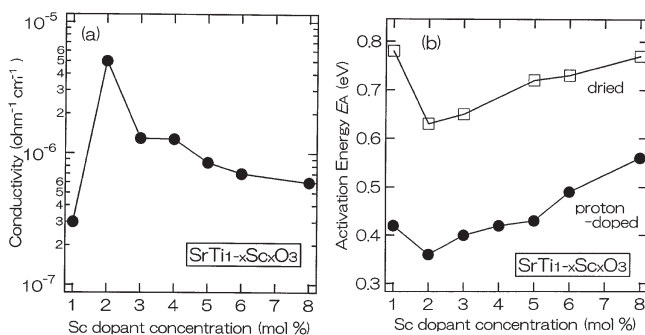
Fig. 2. (a) Electrical conductivity at about 100°C and (b) E_A, estimated from the slope of the Arrhenius plot, against Sc^{3+} dopant concentration. As a reference, the E_A of dried $SrTi_{1-x}Sc_xO_3$ is also shown.[18]

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