PHYSICAL REVIEW B VOLUME 54, NUMBER 22 1 DECEMBER 1996-II

Site identification of protons in $SrTiO_3$: Mechanism for large protonic conduction

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(Received 6 June 1996)

It is found that the proton is strongly absorbed in heavily Sc-doped $SrTiO_3$. Neutron-diffraction measurements were performed using single crystals. The O-H distance is found to be about 1.2 Å and the proton concentration is estimated to be about 2 mol % for $SrTi_{0.98}Sc_{0.02}O_3$. Protonic conduction was observed in Sc-doped $SrTiO_3$ by ac-conductivity measurements in wet air, while the hole conductivity was observed in dry air. The proton is bound by the oxygen ion as if the proton makes the hydrogen bond between two oxygen ions, which might be responsible for the high protonic conductivity in this material. [S0163-1829(96)01445-2]

I. INTRODUCTION

It is known that $SrCeO_3$ shows the protonic conductivity at high temperature when acceptor ions are heavily doped in the Ce-ion site.[1] This material attracts many engineers and research workers, because it has a superior protonic conductivity at high temperature. Proton conductors which function at high temperature will have many promising applications such as fuel cells and hydrogen sensors. By using single crystals of $SrCe_{1-x}Yb_xO_3$, it is confirmed that the proton migrates in the bulk rather than the domain wall and that the proton is bounded by the oxygen ion.[2] However, $SrCeO_3$ is not stable at high temperature — a problem for device applications. The single crystal of acceptor-doped $SrZrO_3$ is found to be a protonic conductor as well.[3] Several acceptor-doped perovskite-type oxides have been found to be the protonic conductors so far.

Several studies have been carried out in order to investigate the proton migration mechanism. One can easily replace protons with deuterons or remove them repeatedly without a change of the crystal structure, so that protons are incorporated in the interstitial sites. The protonic conductivity measurement suggests that proton migration is due to the thermal activation process, which is consistent with the isotopic effects between protons and deuterons in the ionic conductivity. The O-H stretching vibration in the infrared-transmission spectrum suggests that the protons migrate by hopping from site to site near the oxygen ions in the crystal. The O-H stretching vibration is about 3500 cm^{-1} for undoped or slightly doped crystals, while it is about 3200 cm^{-1} and 2500 cm^{-1} for heavily doped ones. It is curious that the heavy doping brings about the high conductivity. It is known that the perovskite-type oxide cannot always become a proton conductor even if the crystal is heavily doped with acceptor ions. For example, Y-doped $BaTiO_3$ hardly shows proton conductivity.[4] This fact suggests that the proton conductivity is not only due to the heavy doping but also due to some important factors which are essential for this type of proton conductor.

The microscopic mechanism has not been studied yet for acceptor-doped perovskite-type protonic conductors. It has been a serious problem that the proton site in these protonic conductors is not known. One cannot discuss how the proton migrates in crystals without knowing where the proton exists. Numerous infrared-transmission and Raman-scattering studies have been carried out for pure or slightly doped $SrTiO_3$ in order to know the symmetry of the proton site.[5–7] The proton site was investigated for pure or slightly doped $SrTiO_3$ in these studies. Two models for the proton site have been proposed. One is between two oxygen ions, which is called the ‘‘octahedron-edge site,’’ and the other is between oxygen and strontium ions, which is called as the ‘‘cube-face site.’’ The proton site in this proton conductor, however, should not be necessarily the same as that in pure or slightly doped $SrTiO_3$, because the absorption structure due to the O-H stretching vibration is very different from those in $SrTiO_3$, as discussed later in this paper. The proton site in heavily acceptor-doped $SrTiO_3$ should be investigated in order to elucidate its role in the proton conducting mechanism.

In this study, neutron-diffraction measurements were carried out in order to investigate the proton site. Thermal neutrons are a sensitive probe for the proton, which allows direct determination of the proton site. In the perovskite-type oxides, $SrTiO_3$ is one of the most suitable materials to study the proton site, because its crystal structure is very simple. The high protonic conduction of $SrTiO_3$ has not been confirmed, though it absorbs the proton to some extent. In this study, it is found that the proton is absorbed in $SrTiO_3$. The result is based on infrared-transmission measurements in the energy region of the O-H stretching vibration when the Sc^{3+} ion is heavily doped into the Ti^{4+}-ion site. The high protonic conduction is confirmed by ac-conductivity measurements.

II. EXPERIMENTS

The sample was prepared by the solid state reaction of $SrTiO_3$, $SrCO_3$, and Sc_2O_3 at 1250 °C for about 15 h, and then single crystals were grown by the floating-zone method using an imaging furnace. The Sc^{3+} ion is found to be doped as an acceptor ion in the Ti^{4+}-ion site of $SrTiO_3$ by a simple thermoelectromotive force experiment.[8] The crystal for neutron diffraction is about 7.5 mm in diameter and 15 mm in length and the dopant concentration is 2 and 3 mol %. Protons are introduced into the crystal by annealing in an atmosphere of wet air or hydrogen gas. It is found that the concentration is largest when the sample is annealed at 300–500 °C in water vapor saturated at a temperature above 90 °C. Heavy water was used in the same way to substitute the proton with the deuteron. We can remove protons or deuterons easily by annealing in dry air above 500 °C for several hours. In this study, the notation of ''H_2O,'' ''D_2O,'' and ''dry'' designates the atmosphere in which the sample was treated. For example, H_2O denotes that the sample was annealed or measured in wet air.

Neutron diffraction was performed with the FOX spectrometer installed at the pulsed spallation neutron facility KENS, Tsukuba, to determine the proton site. The FOX is a time-of-flight (TOF) spectrometer with 128 position-sensitive detectors.[9,10] The sample crystal was placed on the head of a four-cycle goniometer with a special sample holder at a reproducible position. The experiment was performed in air at room temperature.

The conductivity measurement was performed with an impedance analyzer and the conductivity was determined by the cole-cole complex impedance plot at each temperature.

III. RESULTS

A. Neutron diffraction

Neutron-diffraction measurements of proton-doped and deuteron-doped $SrTiO_3$ were carried out in order to determine the proton site. The difference of the scattering intensity for both compounds corresponds to the difference of the structure factors. If one uses the theoretical calculations by using some model of the proton site, the Bragg intensity is obtained by

$$I(h,k,l)=ki(\lambda)|F(h,k,l)|^2L(\lambda,\theta)A(\lambda,\theta)E(\lambda), \tag{1}$$

where I, F, i, L, A, and E are the Bragg intensity, structure factor, incident neutron intensity, Lorentz factor $(=\lambda^4/\sin^2\theta)$, absorption factor, and detector efficiency, respectively. The difference of the structure factors between the proton and the deuteron is small, because the proton/deuteron concentration is small. If we measure the Bragg intensity under the same experimental conditions where these factors except the structure factor are equivalent, the ratio of the Bragg intensity becomes

$$\frac{I_{\text{host+deuteron}}}{I_{\text{host+proton}}}=\frac{|F_{\text{host}}+F_{\text{deuteron}}|^2}{|F_{\text{host}}+F_{\text{proton}}|^2}=\left|1+\frac{F_{\text{deuteron}}-F_{\text{proton}}}{F_{\text{host}}+F_{\text{proton}}}\right|^2. \tag{2}$$

Here, F_{host}, F_{deuteron}, and F_{proton} denote the structure factors of host, deuteron, and proton respectively, and $I_{\text{host+deuteron}}$ and $I_{\text{host+proton}}$ are the Bragg intensities of the samples which are doped with deuterons or protons. One can compare the diffraction intensity ratio with the theoretical calculations for the appropriate models of the proton site. In this study, the difference of the structure factors, $(F_{\text{deuteron}}-F_{\text{proton}})/(F_{\text{host}}+F_{\text{proton}})$, is used to compare experimental results with model calculations.

The structure factor with the indices of the plane (hkl) for the host crystal becomes

$$\begin{aligned}F_{\text{host}}(h,k,l)=b_{\text{Sr}}+(b_{\text{Ti}}C_{\text{Ti}}+b_{\text{Sc}}C_{\text{Sc}_{\text{Ti}}})\exp\pi i(h+k+l)\\+b_{\text{O}}(1-C_{\text{V}_{\text{O}}^{\cdot\cdot}})\{\exp\pi i(h+k)+\exp\pi i(k+l)\\+\exp\pi i(l+h)\},\end{aligned} \tag{3}$$

where b_j is the scattering length of atom j and C_{Ti}, $C_{\text{Sc}_{\text{Ti}}}$, and $C_{\text{V}_{\text{O}}^{\cdot\cdot}}$ are the concentration of Ti, Sc, and oxygen vacancy, respectively. The structure factor for the proton is

$$F_{\text{proton}}=\frac{b_HC_p}{N}\sum_j^N\exp 2\pi i(hx_j+ky_j+lz_j), \tag{4}$$

where C_p is the concentration of the proton and N is the number of equivalent proton sites.

The scattering lengths of the proton and the deuteron are -3.739 and 6.672 ($\times10^{-13}$ cm), respectively, and the structure factors of the proton or the deuteron in the crystal are proportional to their scattering lengths. A better method for estimating the difference of the structure factors is to compare the proton-doped sample with the deuteron-doped one with the assumption that both the proton and deuteron lie at equivalent positions. This assumption may not be so unreasonable, because the crystal structure in the vicinity of the proton does not change much. The ratio of the O-H and the O-D stretching frequencies is close to $\sqrt{2}$, as shown in the next section.

Since infrared-transmission measurements show that the proton is bound by the oxygen ion, two models have been proposed for the proton site in $SrTiO_3$. One is the ''cube-face site''[7] between O-Sr ions as shown in Fig. 1(c). Another is the site in double-minimum potential between O-O as shown in Fig. 1(a). Here, we use ''hydrogen-bond site'' rather than the ''octahedron-edge site'' to emphasize the importance of the hydrogen bond. Since $SrTiO_3$ has the cubic structure, the former includes 12 equivalent positions in the unit cell and the latter includes 24 equivalent positions.

We preferred to observe the scattering intensity at the $(h00)$ planes rather than the other planes, because the $(h00)$ planes give us the most useful information. To compare with experimental values, the structure factors were calculated with many values of O-H length and proton concentration, etc., for the two models. Figure 1 shows several examples for 1 mol % proton concentration. Since the scattering intensity is the largest at (200) in the experiment, the

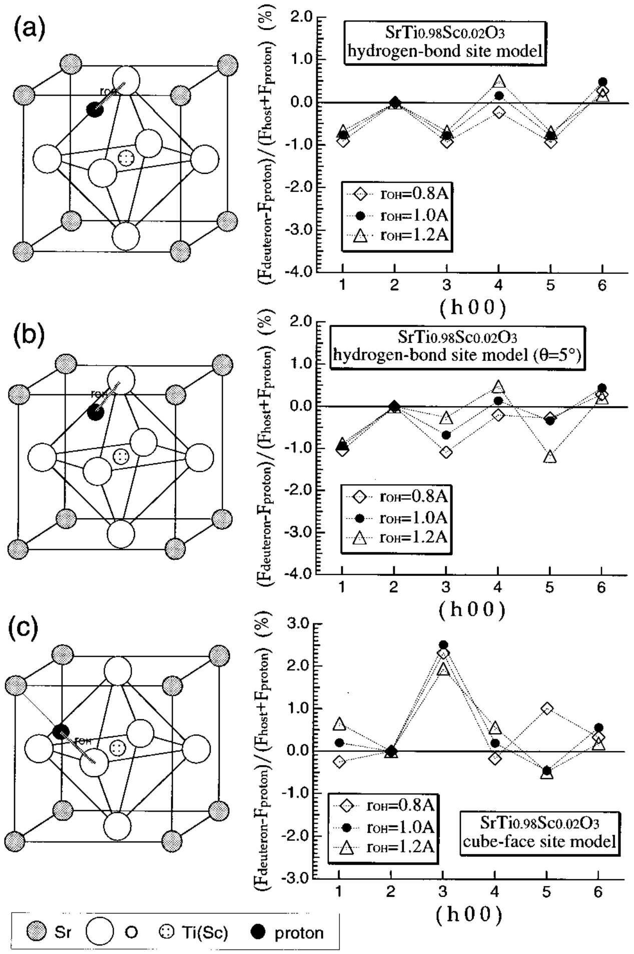

FIG. 1. The three model sites of proton and the differences of the structure factors in $SrTi_{0.98}Sc_{0.02}O_3$. (a) The hydrogen-bond site in which the proton is located in the oxygen octahedra. (b) The hydrogen-bond site in which the proton is slightly leaned to the Ti ion site. (c) The cube-face site in which proton is in the line of O-Sr bond. The O-H distances for these models are 0.8, 1.0, and 1.2 Å.

intensity of the other planes is normalized by the intensity at (200) plane for the both $I_{\text{host+deuteron}}$ and $I_{\text{host+proton}}$. In that case, the difference of the structure factors is always zero at the (200) plane. It is found that there is the simple rule that the calculated difference of the structure factors, $(F_{\text{deuteron}}-F_{\text{proton}})/(F_{\text{host}}+F_{\text{proton}})$, is the same at the even index h for both models. Thus, we should consider only the odd h in order to make clear the difference for both models. Furthermore, in the case of the hydrogen-bond site, all the calculated values at the odd h are $-b_H C_p/3$ independent of h, if the proton is in the straight line between the O-O ions. If the proton is out of the line between the O-O ions, these calculated values at the odd h become different from each other.

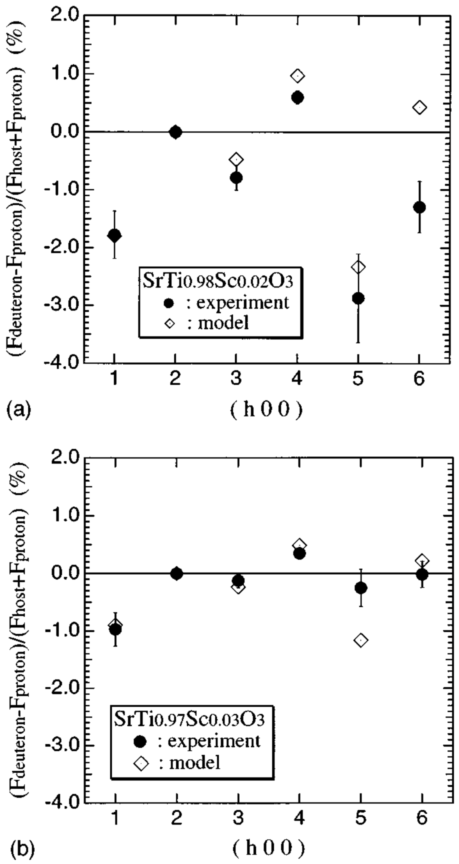

FIG. 2. The difference of the structure factors in $SrTi_{1-x}Sc_xO_3$ for (a) $x=0.02$ and (b) $x=0.03$. The intensities are normalized by that at (200) plane. Then, the difference of the structure factors is always zero at (200). Solid circles represent the experimental results and open diamonds represent the results calculated by the hydrogen-bond site model.

Experimental results of the difference of the structure factors for the (h00) planes are shown in Fig. 2. The solid circles stand for the experimental data. The open diamonds stand for the calculated values, which seems to be the most suitable for the experimental results. The calculated model is based on the ''hydrogen-bond site.'' In the case of the ''cube-face-site'' model, the calculated difference of the structure factors are not fitted at all to the experimental values. The length of O-H is 1.2 ±0.095 Å and the proton concentration is 2.0 ±0.65 mol %. Here, one should notice that the experimental values are not the same at the odd h. This fact corresponds to that the O-H line lean toward the Ti (Sc) site from the O-O straight line by an angle of 5°±3.5°. Figure 3 shows the proton position obtained by the experimental results.

One finds the calculated values for the (100) – (500) planes are fitted well, while the value for the (600) plane is not fitted well. This may be because the width of the Bragg reflection from the higher plane is so wide in the TOF spectrum that the profile cannot be determined accurately.

The neutron-diffraction measurements were also performed for the crystal with the dopant concentration of 3 mol % as shown in Fig. 2(b). The site of the proton is also confirmed with similar results, though the proton concentration for this material is found to be about 1 mol %. The proton concentration of the $SrTi_{0.97}Sc_{0.03}O_3$ is smaller than that of the $SrTi_{0.98}Sc_{0.02}O_3$. This fact is consistent with the dopant dependence of the conduction measurement of $SrTi_{1-x}Sc_xO_3$, which will be published elsewhere.

B. Infrared absorption

Figure 4 shows the infrared-transmission spectra in the energy region of O-H stretching vibration. The thickness of

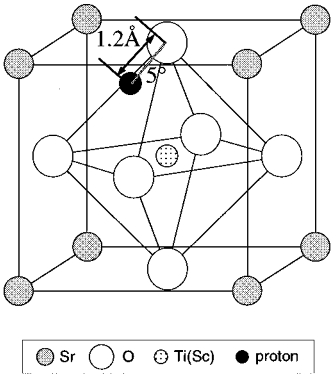

FIG. 3. Crystal structure of $SrTiO_3$ and the proton at the hydrogen-bond site decided by the neutron diffraction. The O-H distance is 1.2 ±0.095 Å and the angle between the O-H and O-O lines is 5°±3.5° and the concentration of proton is 2.0 ±0.65 mol % for $SrTi_{0.98}Sc_{0.02}O_3$ and 1 mol % for $SrTi_{0.97}Sc_{0.03}O_3$.

the sample is 0.7 mm for the $SrTi_{0.97}Sc_{0.03}O_3$ and 2.0 mm for the undoped $SrTiO_3$. The absorption intensity of $SrTi_{0.97}Sc_{0.03}O_3$ is much stronger than that of undoped $SrTiO_3$ in the O-H stretching vibration region. The O-H stretching energy in undoped $SrTiO_3$ is about 3500 cm^{-1}, which is very close to the free O-H stretching energy. The absorption of O-H stretching of undoped $SrTiO_3$ is very weak and narrow. In the case of $SrTi_{0.97}Sc_{0.03}O_3$, the O-H stretching vibration was observed at 3300 cm^{-1}. Protons are easily exchanged into deuterons by the annealing in heavy water vapor. The O-D stretching vibration was observed at 2437 cm^{-1} for the sample which was annealed in heavy-water vapor. There is no structure in the energy region of the O-H stretching vibration for the sample which was annealed in dry air. By the infrared-transmission measurement, it is confirmed that the proton or deuteron is absorbed strongly in $SrTi_{0.97}Sc_{0.03}O_3$ compared with undoped $SrTiO_3$. Furthermore, this stretching energy becomes lower than that of undoped $SrTiO_3$.

Obviously, the heavy doping is responsible for the high proton concentration in the crystal and the weakness of the O-H binding energy. The ratio of the vibration frequencies $\nu_{\text{O-H}}$ and $\nu_{\text{O-D}}$ is approximately $\sqrt{2}$ which is the square root of the mass ratio. The existence of absorption due to O-H vibration implies that the proton is attached to the oxygen ion in the crystal. This fact is quite consisted with the neutron measurements. The absorption structure due to O-H stretching vibration is rather narrow in $SrTi_{1-x}Sc_xO_3$ compared with acceptor-doped $SrCeO_3$ or $SrZrO_3$. This fact may reflect that the crystal structure of $SrTiO_3$ is simple. Those of $SrCeO_3$ and $SrZrO_3$ are complicated, so that they may consist of several different O-H lengths.

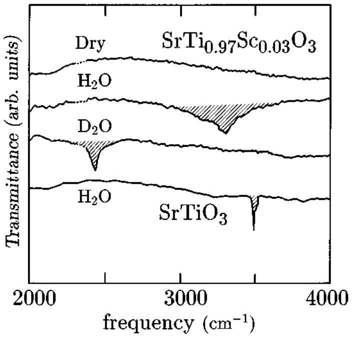

FIG. 4. Infrared-transmission spectra of $SrTiO_3$. The sample was annealed in three different atmospheres. The dry, H_2O, and D_2O stand for the atmospheres of dry air, water vapor, and heavy-water vapor. The sample thickness of $SrTi_{0.97}Sc_{0.03}O_3$ is 0.7 mm and that of $SrTiO_3$ is 2.0 mm. In $SrTi_{0.97}Sc_{0.03}O_3$, absorptions due to O-H and O-D stretching vibrations are observed at 3300 and 2437 cm^{-1}. The sharp structure of O-H stretching vibration is observed at about 3500 cm^{-1} in undoped $SrTiO_3$.

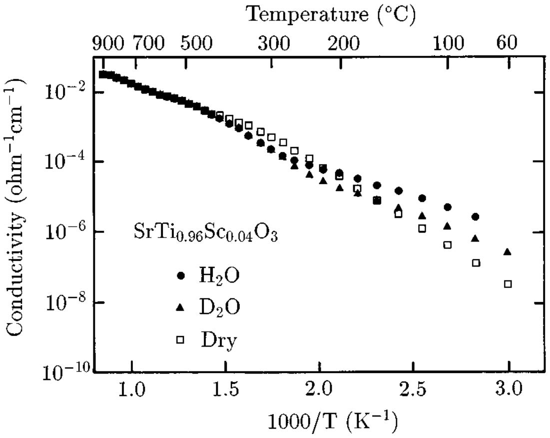

FIG. 5. Arrhenius plot of electric conductivities in the three different atmospheres. Below 200 °C, the conductivity of proton is larger than that of the deuteron, which suggests that the proton or deuteron migrates by hopping from site to site in Sc-doped $SrTiO_3$.

C. Protonic conduction

Figure 5 shows the Arrhenius plot of the conductivity measured in dry air, water vapor, and heavy-water vapor saturated at 90°. Conductivities in water vapor are always higher than in heavy-water vapor. The conductivities in water vapor below 200 °C become larger than those in dry air. In this temperature region, it is clear that protons migrate by hopping from site to site. The conductivity ratios of the proton and the deuteron are approximately the inverse of the mass ratio. Above 400 °C, the conductivities are almost the same values for the three atmospheres. The conductivity is a little higher in dry air from 300 to 400 °C than in water–heavy-water vapor. Above 400 °C, the electrical conduction was mainly due to holes or oxygen vacancies rather than protons or deuterons. These features are observed similarly for other perovskite-type oxides which conduct protons well.[3] The transition temperature from the hole to the proton is much lower than the other protonic conductors, such as $SrCeO\text{-}_3$- and $SrZrO_3$-based compounds.

IV. DISCUSSION

In this study, the distance of O-H is evaluated to be 1.2 Å, while that of O-O is 2.76 Å. This is the surprising fact, because this O-H distance is extremely longer than the free O-H distance of about 0.96 Å. This O-H distance should be compared with the values of the various materials which belong to the hydrogen-bonded materials. Novak has shown the empirical relation between the O-H distance and O-H stretching vibration.[11] By this relation, 1.2 Å corresponds to the O-H vibration of 1000 cm^{-1}. In fact, the O-H stretching vibration of this material in Fig. 4 is rather weak compared with the free O-H stretching vibration. In the scheme of Novak, this material belongs to the strong hydrogen-bonded material. Of course, this relation can not be simply applied to $SrTi_{1-x}Sc_xO_3$ because the O-H stretching vibration is also a function of the O-O distance, which is determined by the host material in the case of $SrTi_{1-x}Sc_xO_3$.

According to a simple interpretation the hydrogen bond is caused by the mechanism that the proton is attracted by the oxygen ion which is located at the opposite side to the bound oxygen ion. Even in the perovskite-type oxides, it is found that this mechanism is important. It is reasonable that the protonic conduction is responsible for the weakness of the O-H binding energy due to the similar mechanism to the hydrogen bond.

It is also found that the proton is off the straight line of two oxygen ions and slightly close to the Ti- (Sc-) ion site. This fact may reflect that the proton is attracted by the Sc^{3+} ion, because Sc^{3+} ion in the Ti^{4+}-ion site acts as a negative ion to the proton and the neutron diffraction feels the average potential of the both Sc^{3+} and Ti^{4+} ions in the crystal.

V. CONCLUSION

$SrTiO_3$ exhibits a significant protonic conductivity when it is heavily doped with the Sc ion. The proton concentration is 2 ±0.65 mol % for $SrTi_{0.98}Sc_{0.02}O_3$. Protons hop from site to site below 300 °C in the wet air. According to the neutron-diffraction measurement, the proton is determined to be in the site between the O-O ions which consist of an oxygen octahedron, as if it forms the hydrogen bond. It is supposed that the protonic conductivity increases when the strength of O-H bond becomes weak due to the property of the hydrogen-bond effect.

ACKNOWLEDGMENTS

This research was supported by the Grant-in-Aid for Scientific Research on Priority Areas (No. 260) from The Ministry of Education, Science, Sports and Culture, Japan.

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