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Proton Diffusion in $SrZr_{0.95}Y_{0.05}O_3$ Observed by Quasielastic Neutron Scattering

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Proton diffusion was observed in Y-doped $SrZrO_3$ ceramics above 500°C by quasielastic neutron scattering. The line width of the quasielastic component varies with energy transfer Q and temperature. The temperature dependence is well elucidated by the thermal activation-type proton migration with activation energy of 0.2 eV. The observed hopping distance was 1.7 Å, which is comparable to one of the distances between two proton sites.

KEYWORDS: proton conductor, perovskite-type oxides, quasielastic neutron scattering

§1. Introduction

Proton conducting ceramics, like $SrCeO_3$, was found in the early 1980's.[1)] These proton conducting oxides, which are also known as high temperature-type proton conductors, are studied for application to various devices such as fuel cells and hydrogen sensors at high temperatures. In addition with these applicational studies, proton dynamics are investigated from physical points of view.

It is interesting that some perovskite-type oxides show high proton conductivity when they are doped with a few mol% trivalent cations, while protons are not mobile at all in those undoped oxides, that is, those undoped oxides are not proton conductors by themselves.

Shin *et al.* showed that protons migrate in bulk crystal of $SrZr_{0.95}Y_{0.05}O_3$ rather than in domain wall by studies on proton conductivity using single crystals.[2,3)] The electrical conductivity shows the thermal activation-type behavior at the temperature region from 300 K to 1200 K and shows that the main carrier is proton below 1000 K. They confirmed that protons are bounded by oxygen ions in the crystal from infrared absorption spectra.[3)] The frequency of O-H stretching vibration in the protonic conductor is less than that in H_2O molecule by 300 to 1000 cm^{-1}, while those in undoped perovskite-type oxides are close to that in H_2O molecule. They suggested that protons are bounded by two oxygen ions as if they make hydrogen bonds in oxygen-octahedron and this makes protons mobile in the crystal. It is reported that the high proton mobility is due to the hydrogen bonds in oxide glasses.[4,5)] In the pure or slightly doped $SrTiO_3$, it is supposed that proton is situated in between O-O by polarized infrared measurements[6)] and Raman scattering study.[7)] Neutron diffraction also supports this suggestion for heavily Sc-doped $SrTiO_3$.[8)]

Matke *et al.* reported the observation of proton diffusion in Yb-doped $SrCeO_3$ by quasielastic neutron scattering.[9)] They proposed two-state model, that is, free diffusion and trap states. In this model, proton migrates with successive jumps, trapping near an Yb^{3+} ion and escaping from the trapping state.

Recently, Shimojo *et al.* reported first principles calculation of proton motion in $SrTiO_3$[10)] and $SrCeO_3$.[11)] They found two kinds of proton motion in the simulation: one is O-H stretching vibration between two oxygen ions, the other is rotation of O-H bond around the oxygen ion.

It's very important for illustrating the migration mechanism to investigate proton conduction from microscopical points of view. Proton has large scattering cross section with thermal neutron, and neutron scattering will play a powerful role to investigate these proton conducting oxides. In this study, quasielastic neutron scattering (QENS) study on Y-doped $SrZrO_3$ has been performed to reveal proton migration mechanism.

§2. Experiment

2.1 Sample

The sample was sinterd ceramics prepared by solid state reaction of $SrCO_3$, ZrO_2 and Y_2O_3 at 1300°C, and pressed into cylinder of ϕ13mm×80mm, then sinterd again in air at 1300°C for 20 hours. It was annealed in wet air below 1000°C for several hours to introduce protons into the crystal. The sample container was made of stainless steel and container thickness is about 0.5mm. The sample container was purged by Ar gas and then it was sealed by an o-ring of stainless steal to avoid leaking of hydrogen gas from the container. It is reported that proton concentration in $SrCeO_3$ based proton conducting ceramics is at most 4 mol%.[12)] Proton concentration in $SrZrO_3$ based proton conductor is estimated from infrared absorption to be about 1~2 mol% on the analogy of that in $SrCeO_3$.

2.2 Quasielastic neutron scattering

The QENS spectra were obtained by the time-of-flight (TOF) spectrometer LAM40 installed at the pulsed spallation neutron facility KENS, Tsukuba. The LAM40 an-

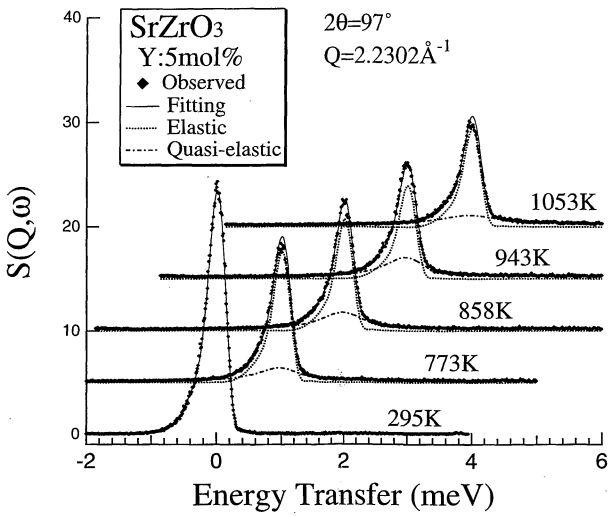

Fig. 1. The scattering function at several temperature of $Q = 2.2302\,\text{Å}^{-1}$. The solid line represents the results of the fitting, the dotted line represents the elastic component and the broken line represents the QENS component. The origins of the both axes are shifted toward upper right.

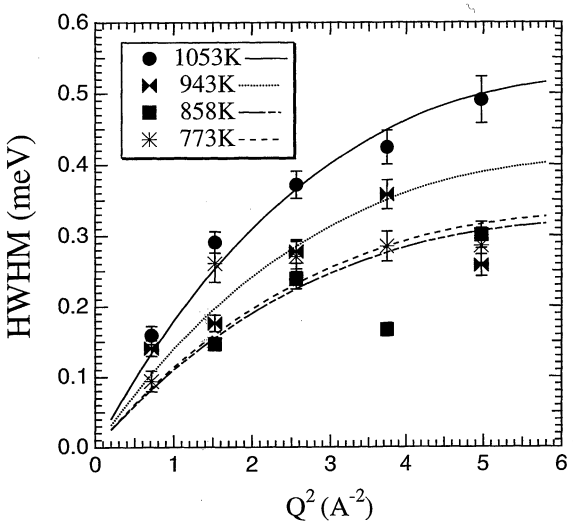

Fig. 2. Q-dependence of HWHM of quasielastic scattering from proton diffusion at several temperatures. The markers represent HWHM and the lines represent fitting results to eq. (1) with hopping distance l of 1.7 Å.

alyzes the TOF-spectra with inverse geometry and has the seven analyzer mirrors and detectors which covers over $0.2 < Q < 2.7\,\text{Å}^{-1}$, with the energy resolution of $200\,\mu\text{eV}$.

The measurements were carried out at 295 K, 573 K, 773 K, 858 K, 943 K and 1053 K. The sampling time was about 20 hours at each temperature. The sample temperature was controlled with electric heater at the both ends of the container. After the experiments, QENS spectra were measured again at 573 K and it is observed that the scattering intensity did not change after heating for a few days, so it was confirmed that the proton concentration in the sample was not changed.

The spectra were analyzed by the least-square fitting to model functions using SALS (Statistical Analysis with Least Squares fitting) system. The resolution function was determined with the spectrum at 295 K, where quasielastic component was not observed, and its shape is identical to that of vanadium. The resolution function is not symmetric as shown in Fig. 1. This asymmetric shape of the resolution function is the characteristics of this apparatus.

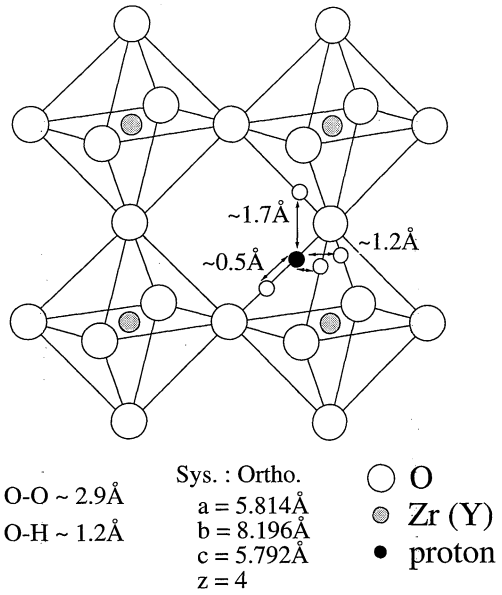

Fig. 3. Proton sites determined by neutron diffraction of $SrTi_{1-x}Sc_xO_3$. To illustrate the proton diffusion, four possible directions to jump in the lattice are estimated for $SrZrO_3$ on the analogy of the structure of $SrTiO_3$.

§3. Results and Discussion

Figure 1 shows the quasielastic neutron scattering with $Q = 2.2302\,\text{Å}^{-1}$ at several temperature. It is clear that the peak height of $S(Q,\omega)$ decreases as the temperature increases and the linewidth increases with increasing temperature. The spectrum broadening was not observed at 573 K except for decrease of total intensity. The decreasing intensity is due to the temperature dependence of the elastic scattering.

The temperature dependence suggests that there should be a quasielastic component in these spectra above 573 K. It is reasonable that the spectrum at a temperature above 573 K was fitted by deconvolution of three components: elastic scattering (the spectrum shape of this component is the same as the resolution function), quasielastic scattering (explained by Lorentzian) and constant background.

By the hopping model of proton migration in powder sample, it is well known that the quasielastic component becomes a Lorentzian with a width of

$$\Gamma = \frac{1}{\tau} \cdot [1 - \frac{\sin Ql}{Ql}], \tag{3.1}$$

where τ is the relaxation time and l is the hopping distance.[13] The spectrum was deconvoluted with the resolution function, assuming that the spectra consist of QENS, elastic scattering and constant background. The fitting results of the half width at half maximum (HWHM) are plotted in Fig. 2 as a function of momentum transfer Q. For small Q, the HWHM obeys the Q^2

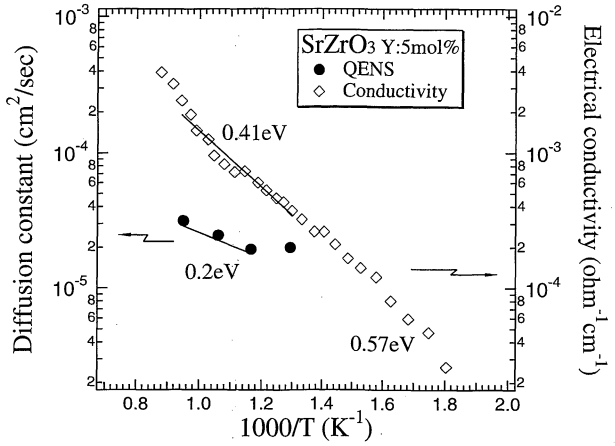

Fig. 4. The Arrhenius-plots of self-diffusion constants calculated from QENS and AC electrical conductivities measured in wet air.

law as led from eq. (3.1).

$$\Gamma \cong \frac{Q^2 l^2}{\tau}, \tag{3.2}$$

The Q-dependence of HWHM can be explained by eq. (3.1) with $l = 1.7$ Å in this study. From neutron diffraction study, it is known that proton is situated at 24-equivalent sites in between two adjacent oxygens of the octahedron in a perovskite unit cell in Sc-doped $SrTiO_3$. It is presumable that the proton is in such a site in $SrZrO_3$ as illustrated in Fig. 3 on the analogy of the results about $SrTiO_3$. Consequently, the hopping distance of 1.7 Å corresponds to a direction between two oxygen octahedrons, as shown in this figure. Of course, it is supposed that proton may jump to another direction with a less distance such as 0.5 Å and 1.2 Å. The proton hopping between two oxygen ions with a distance of 0.5 Å is necessary for proton migration. However, the HWHM of the scattering spectrum for other hopping distance is much less than that observed here, because Γ is proportional to l^2. If l is smaller than 1.7 Å, it is difficult to observe the elastic component because of the resolution. Thus, it is difficult to separate them with this resolution.

So far, the results obtained in this study suggest that proton hopping model in the crystal was confirmed and proton hopping with distance of 1.7 Å was observed.

The Self-diffusion constants were calculated by τ and l,

$$D = \frac{l^2}{6\tau}. \tag{3.3}$$

The results are shown in Fig. 4 together with the electrical conductivity. Their activation energies estimated from these slopes are 0.2 eV for self diffusion constant and 0.57 eV for electrical conductivity. Their behaviors resemble qualitatively. This is because D is proportional to σ, as shown by the following equation,

$$D \propto \frac{T \cdot t_p}{C_p}\sigma, \tag{3.4}$$

where t_p is the transport number of proton and C_p is the proton concentration. The difference between those two slopes shows that the transport number of proton (t_p) decreases with increasing temperature or proton concentration (C_p) increases with increasing temperature. Therefore, it is suggested that above 500°C proton conductivity changes more gently than the electrical conductivity and then the activation energy of proton should be less than 0.57 eV. Since it is known that C_p and t_p decreases as the temperature increases in those type of proton conductors, it is clear that t_p decreases above 500°C due to the increasing of hole conduction.

The integrated intensities of elastic and quasielastic components decrease with increasing temperature. It is supposed that the decrease in the elastic intensity is due to the temperature dependence, as mentioned above, and the decrease in the quasielastic intensity is due to the temperature dependence of the proton concentration in the crystal.

§4. Conclusion

In conclusion, it is confirmed that proton diffusion in perovskite-type oxides can be explained by the hopping model from QENS study. The observed hopping distance was 1.7 Å. From the temperature dependence between 773 and 1053 K, the activation energy for proton hopping observed in this study was determined to be 0.2 eV. This value is much smaller than that determined from electrical conductivity. Higher resolution and at higher Q values are necessary for more precise investigation.

1) H. Iwahara, T. Esaka, H. Uchida and N. Maeda: Solid State Ionics **3/4** (1981) 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) 910–913.
4) Y. Abe, H. Hosono, Y. Ohta and L. L. Hench: Phys. Rev. B **38** (1988) 10166.
5) Y. Abe, H. Hosono, W. Lee and T. Kasuga: Phys. Rev. B **48** (1993) 15621.
6) G. Weber, S. Kapphan and M. Wöhlecke: Phys. Rev. B **34** (1986) 8406.
7) S. Klauer and M. Wöhlecke: Phys. Rev. Lett. **68** (1992) 3212.
8) N. Sata, K. Hiramoto, S. Shin, S. Hosoya, N. Niimura and M. Ishigame: Phys. Rev. B **54** (1996) 15795.
9) Th. Matke, U. Stimming, Ch. Karmonik, M. Soetratmo, R. Hemplemann and F. Güthoff: Solid State Ionics **86–88** (1996) 621.
10) F. Shimojo, K. Hoshino and H. Okazaki: J. Phys.: Condens. Matter **10** (1998) 285–294.
11) F. Shimojo, K. Hoshino and H. Okazaki: J. Phys. Soc. Jpn. **67** (1998) 2008–2011.
12) T. Yajima, T. Yogo, H. Iwahara: The 16th Symposium on Solid State Ionics in Japan, Extended Abstracts (1990) 37–38 [in Japanese].
13) G. T. Chudley and R. J. Elliott: Proc. Phys. Soc. **77** (1961) 353.