



# Hole-state and defect structure of proton conductor SrTiO<sub>3</sub> observed by high-resolution X-ray absorption spectroscopy

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## Abstract

The hole-state and defect structure of proton conductor SrTi<sub>1-x</sub>Sc<sub>x</sub>O<sub>3</sub> have been studied by high-resolution X-ray absorption spectroscopy. The proton-induced level is observed in proton-doped SrTi<sub>1-x</sub>Sc<sub>x</sub>O<sub>3</sub>. The energy separation between the top of the valence band and the bottom of the acceptor or proton level is considered to be the activation energy determined by electronic or proton conductivity. © 2000 Elsevier Science B.V. All rights reserved.

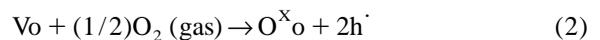
**Keywords:** Protonic conductor; SrTiO<sub>3</sub>; XAS; Hole-state; Proton level; Acceptor level

## 1. Introduction

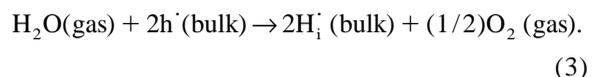
Some perovskite-type oxides, such as SrTiO<sub>3</sub> and SrCeO<sub>3</sub>, become proton conductors when they are doped with a few mol% acceptor ions [1,2]. They are regarded as promising materials for a wide variety of electrochemical applications such as fuel cells and hydrogen sensors, etc. because of their stability at high temperature. When a trivalent cation such as Sc<sup>3+</sup> is doped in a Ti<sup>4+</sup> site, an oxygen ion vacancy is created in the crystal for charge compensation. That is,



where Sc'<sub>Ti</sub> indicates Sc<sup>3+</sup> ion in the Ti<sup>4+</sup> site and Vo indicates oxygen ion vacancy in Kroger–Vink notation. In the hole-proton exchange model, an oxygen vacancy is filled by an oxygen ion by annealing in air and a hole is formed in the crystal:



where O<sup>xo</sup> indicates oxygen ion in the oxygen site and h<sup>·</sup> indicates a hole in the crystal. Thus, H<sub>2</sub>O gas resolved at the surface and a proton is formed by exchanging with a hole in the crystal:



In order to investigate the proton migration mech-

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anism, several studies of electronic structure have been performed on Sc-doped  $\text{SrTiO}_3$  and Yb-doped  $\text{SrCeO}_3$  [3]. It has been reported that the band structure of protonic conductor  $\text{SrTiO}_3$  obeys the rigid-band model [4]. Furthermore, it has been indicated that the hybridization effect between the Ti  $3d$  and O  $2p$  states is also important for protonic conductivity [5].

The electronic structure near the  $E_F$  gives an important information for the mechanism of protonic conduction. In this paper, the electronic structure in the band gap energy region has been studied by high resolution X-ray absorption spectroscopy.

## 2. Experimental

The sample was prepared by the solid state reaction of  $\text{SrTiO}_3$ ,  $\text{SrCO}_3$  and  $\text{Sc}_2\text{O}_3$  at  $1250^\circ\text{C}$  for about 15 h. The single crystals were grown by the floating-zone-method using Xe-arc imaging furnace. The crystals were examined using X-ray diffraction. Protons were introduced into the crystal by annealing in an atmosphere of  $\text{O}_2 + \text{H}_2\text{O}$  ( $P_{\text{O}_2} = 0.49$ ,  $P_{\text{H}_2\text{O}} = 0.03$ ) above  $900^\circ\text{C}$  for 15 h.

The experiments were carried out at undulator beamline BL-19B in the Photon Factory at High Energy Accelerator Research Organization, Tsukuba in Japan. Synchrotron radiation from the undulator was monochromatized using a grating monochrometer VLM19 [6]. The resolution of the beamline was smaller than about 0.1 eV at  $h\nu = 500$  eV. The XAS spectra were measured by the XUV silicon photodiode.

## 3. Results and discussion

Fig. 1(a) shows the Sc doping dependence of O  $1s$  XAS spectra for dried  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ , respectively. The abscissa represents energy relative to  $E_F$ . The position of the  $E_F$  is determined by O  $1s$  photoemission peak. The arrow shown in each spectrum is the top of the valence band. From the dipole selection rule, it is indicated that the O  $1s$  XAS spectra of  $\text{SrTiO}_3$  correspond to transitions into O  $2p$  character hybridized into the unoccupied Ti  $3d$  states [7]. The peak around 2 eV is the  $t_{2g}$  subband of the

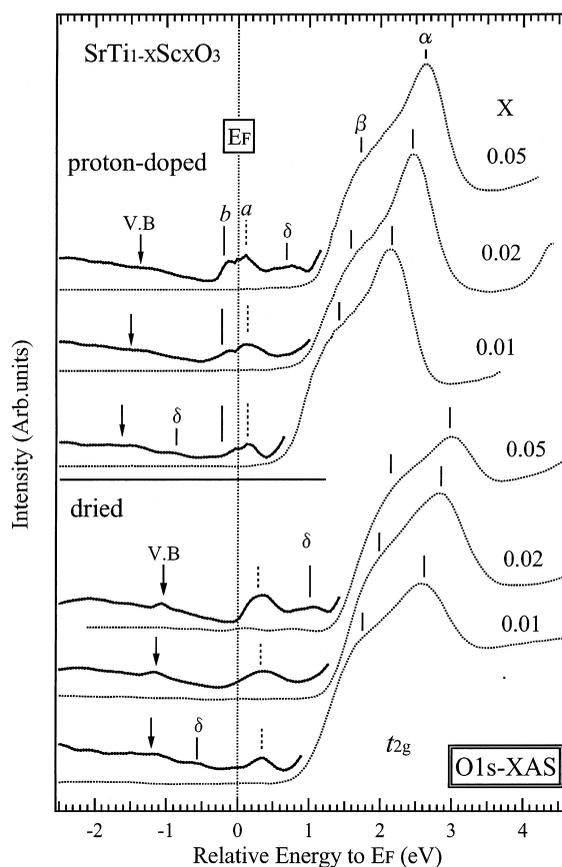


Fig. 1. O  $1s$  XAS spectra of (a) dried and (b) proton-doped  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ . Arrow (V.B.) shows the top of the valence band. Vertical dashed bar shows the position of the Fermi level.

Ti  $3d$  states. The shoulder ( $\beta$  peak) around 1 eV is firstly observed in this study. The intensity of  $\beta$  peak changes with Sc doping. Such behavior is also found in the resonant-photoemission spectra. This is considered to indicate the magnitude of the hybridization effect between Ti  $3d$  and O  $2p$  states.

Fig. 1(b) shows the Sc doping dependence of O  $1s$  XAS spectra for proton-doped  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ . The conduction band and the top of the valence band shift to lower energy by about 1.0 eV in proton-doped  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ . On one hand, this shift indicates that the  $E_F$  shifts to the conduction band side. This shift is contributed that the doped proton acts as donor, when it is introduced into the crystal lattice. Such behavior can be understood by the rigid-band model [4,5].

The intensity of the photon energy region from  $-2$  to  $1$  eV is expanded as solid line above the XAS spectrum in order to obtain the precise information in the band gap region. In dried  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ , two structures  $a$  and  $b$  were observed in the band gap region. Each structure shows the Sc doping dependence. Firstly, the small structure observed near the V.B. is considered to be the hole state created in the top of the valence band. In the absorption spectra of ultraviolet region, the increase of the band gap with Sc doping is explained from the hole state creates in the top of the valence band. This result indicates that the doped hole ( $\text{Sc}^{3+}$ ) is introduced into O  $2p$  orbital. Secondly, a prominent feature  $a$  is observed at the  $E_F$ . In term of the rigid-band model, this feature may be analyzed as the acceptor level. A similar structure has been observed in the absorption spectra of acceptor-doped  $\text{SrZrO}_3$ .

In the O  $1s$  XAS spectra of proton-doped  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ , the hole state of the valence band decreases by proton doping. Furthermore, the hole disappears when Sc dopant is 2 mol%. This indicates that the proton exchanges with the oxygen vacancy and hole in the bulk state (Eq. (3)). On the other hand, two splitting structures are found near the  $E_F$ . The intensity of the acceptor level is lower in proton-doped  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$  and the structure ( $b$ ) below  $E_F$  appeared largely. The  $E_p$  may be the proton level. Although the proton level is occupied by the proton in ground state, this is considered to contribute the thermal excitation of proton.

Fig. 2 shows the energy separation between the top in the valence band and the bottom of the acceptor level in dried and proton-doped  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ . This energy separation is considered to give the activation energy of hole and proton. The activation energy of hole and proton is the lowest when Sc doping concentration is 2 mol%. This result may be consistent with the result obtained from the conductivity measurement [8].

Several small structures ( $\delta$ ) are observed in the band gap energy region. The only considerable factor is the defect structure. Such a structure is not observed in the band gap region when Sc dopant is 2 mol%. This fact, attributed to the defect structure, is occupied by the dopant proton. On the other hand, the decreasing of hole state at the top of the valence band for proton-doped  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$  indicates that

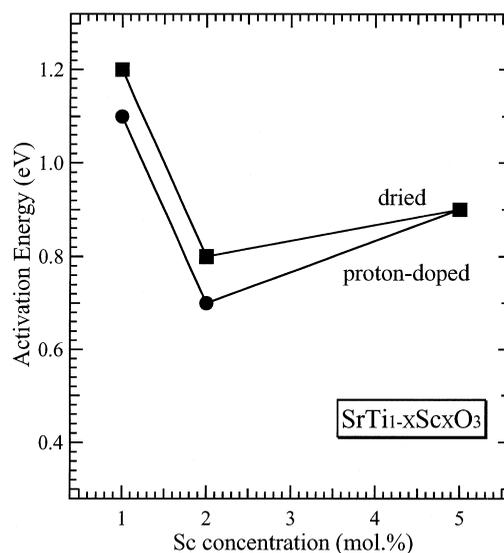


Fig. 2. Energy separation between the top of the valence band and the bottom of the acceptor level in dried and proton-doped  $\text{SrTiO}_3$ .

proton is absorbed by the exchange of hole. However, the existence of defect structure may also be important for the mechanism of protonic conductivity.

#### 4. Conclusion

In this study, we studied the electronic structure in the band gap region of protonic conductor  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$  by high resolution X-ray absorption spectroscopy. Hole states created in the top of the valence band and acceptor level are observed in dried  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ . In proton-doped  $\text{SrTi}_{1-x}\text{Sc}_x\text{O}_3$ , the intensity of hole state in the valence band decreases and proton level was observed near  $E_F$ . This result indicates that proton is absorbed by the exchange of hole.

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