

Photoemission Study on Protonic Conductor CaZrO₃: Evidence of the Exchange Mechanism of Proton and Hole

Tohru HIGUCHI, Takeyo TSUKAMOTO, Yasuhisa TEZUKA¹, Kiyoshi KOBAYASHI²,
Shu YAMAGUCHI³ and Shik SHIN^{4,*}

Department of Applied Physics, Science University of Tokyo, Tokyo 162-0825, Japan

¹Faculty of Science and Engineering, Hirosaki University, Hirosaki 036-8561, Japan

²National Institute of Materials and Chemical Research, Tsukuba 305-8565, Japan

³Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

⁴Institute for Solid State Physics, University of Tokyo, Tokyo 106-8666, Japan

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The exchange mechanism of proton and hole in protonic conductor CaZrO₃ has been investigated by photoemission spectroscopy. The Fermi level is higher by about 1.0 eV through proton doping, indicating that protons exchange with holes. The defect chemical calculation proves that the change of the number of the protons, holes, and the oxygen vacancies by the proton doping accords with the photoemission process.

KEYWORDS: CaZrO₃, photoemission, electronic structure, proton, hole, oxygen vacancy

Some perovskite-type oxides, such as CaZrO₃, SrTiO₃ and SrCeO₃, exhibit remarkable proton conductivity when they are doped with a few mol% of acceptor ions.^{1–3} Oxide-type proton conductors are important materials for a wide variety of electrochemical applications such as fuel cell and hydrogen sensor. Few protonic conductors, however, can be used at high temperature. Among these potential conditional, the most practical protonic conductor is In³⁺-doped CaZrO₃, which shows the proton conductivity stabilized at relatively high temperature.³ The defect chemistry, thermodynamics, electrical and transport properties have been extensively studied.^{4,5} It is reported that the main charge carrier is proton, oxygen ion, hole and the dominant conductivity region changes by the value of oxygen or hydrogen fugacity.⁴ However, the detail of protonic conductivity in CaZrO₃ has not been clarified so far.

A protonic conduction mechanism was investigated with single crystal of Y³⁺-doped SrCeO₃ and Sc³⁺-doped SrTiO₃.^{4,5} The frequency of the O–H stretching vibration has been found in the infrared transmission measurement, indicating proton migration in the bulk state.² Furthermore, it is indicated from the neutron-diffraction that the proton is bound by oxygen ions as if the proton makes the hydrogen bond between two-oxygen ions.⁶ This fact has been also expected from an *ab initio* molecular-dynamics simulation of Shimojo *et al.*⁷ Then, it is proposed that proton migrates by hopping from site to site around the oxygen ion.

Recently, the electronic structure of Sc³⁺-doped SrTiO₃ has been studied by absorption spectra in the vacuum ultraviolet region⁸ and photoemission spectroscopy.^{9,10} The energy shift of absorption edge due to Sc doping was observed. In the photoemission spectra, the top of the valence band shifts to the lower binding energy with increasing Sc doping. These behaviors are in a good agreement with the rigid-band model. On the other hand, it is reported that the Ti 3*d* state hybridizes with O 2*p* state in the valence band and the hybridization effect depends on the electrical conductivity.^{9,10} This effect is also found in the photoemission spectra of Yb³⁺-doped SrCeO₃.¹¹ For these reasons, it may be expected that the band structure and the hybridization effect are related with the pro-

ton conductivity of CaZrO₃.

In this Letter, we present photoemission spectra in the valence band region of protonic conductor CaZrO₃. Although it is supposed in SrTiO₃ and SrCeO₃ that the proton absorption mechanism is closely related to proton conduction because proton must migrate when it is absorbed to the crystal lattice, the mechanism of proton migration of CaZrO₃ has not yet been clarified experimentally. It is discussed in CaZrO₃ how the proton solubility is related with the electronic structure.

The sample was a sintered ceramics prepared by a conventional solid-state reaction method. Starting materials were ZrO₂ of 98% with 1.0 mass% HfO₂ (99 mass% for ZrO₂ + HfO₂) supplied by High Purity Chemicals Inc. (Saitama, Japan) and CaCO₃ of 99.995 mass% and In₂O₃ of 99.999 mass% purity supplied by Rare Metallic Co. Ltd. (Tokyo, Japan). Major impurities of ZrO₂ were analyzed as Ca (800 mass ppm), Mg (200 mass ppm), Si (100 mass ppm), Al (60 mass ppm) and Ti (50 mass ppm). The sample rods, prepared by the isostatic pressing of well-mixed powder of the nominal composition of CaZr_{0.99}In_{0.01}O_{2.995} (ZrO₂ content is indicated by the sum of ZrO₂ and HfO₂), were calcined at 1673 K for 10 h in air. Then, the samples were crushed to powder and mechanically pressed into the disks. Finally, the disks were sintered at 1873 K for 10 h in air. The density of the disks was higher than 98% of theoretical one calculated from the lattice parameter. The samples were confirmed as being of a single phase with the perovskite structure by the powder X-ray diffraction analysis.

Photoemission spectroscopy (PES) spectra were measured at BL-2 of SOR-RING of the Synchrotron Radiation Laboratory, Institute for Solid State Physics (ISSP), University of Tokyo. The kinetic energy of the photoelectron was measured with a double-cylindrical mirror analyzer. The samples were scraped *in situ* with a diamond file in a vacuum of 3.0×10^{-10} Torr in order to obtain the clean surface.

Figure 1 shows the PES spectra in the valence band region between dried (CZ-Dry) and proton-doped CaZr_{0.99}In_{0.01}O_{2.995} (CZ-Wet) measured at $h\nu = 90$ eV, respectively. The valence band spectra have two features shown as A and B, which mainly consist of O 2*p* states mixed with Zr 4*d* states. It is known that the feature A corresponds to the nonbonding state and that the feature B corresponds to

*And also from RIKEN, Hyogo 679-5143, Japan.

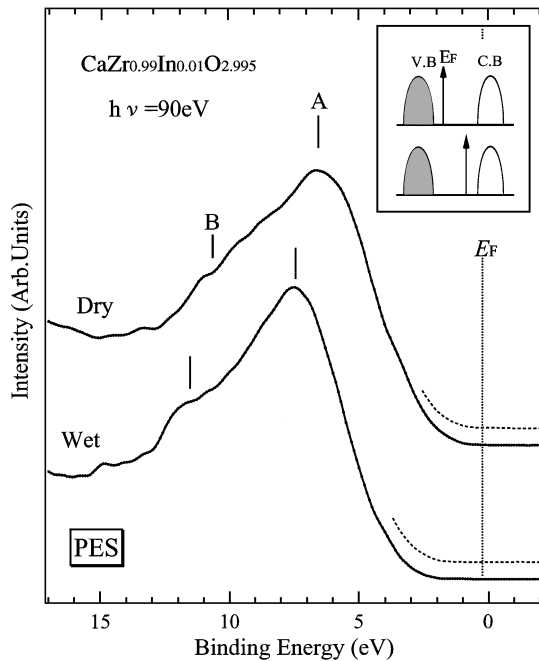


Fig. 1. PES spectra in the valence band region between CZ-Dry and CZ-Wet measured at $h\nu = 90$ eV. Inset shows the schematic diagrams of E_F position of CZ-Dry and CZ-Wet. Dashed lines show the PES spectra in the band gap energy region on an expanded scale.

the bonding state that is well mixed with the Zr 4d states. These peak positions are different in CZ-Dry and CZ-Wet. The features A and B are observed at ~ 6.5 and ~ 11.2 eV in CZ-Dry, while these are observed at ~ 7.5 and ~ 12.2 eV in CZ-Wet. Therefore, the valence band of CZ-Dry shifts to the lower binding energy by about 1.0 eV, indicating the shift of Fermi level (E_F) by the decrease in the hole concentration. On the other hand, dashed lines show the PES spectra in the band gap energy region on an expanded scale for CZ-Dry and CZ-Wet. The existence of the proton-induced level could not be observed in both samples.

Inset of Fig. 1 shows a schematic diagram of E_F position. The band gap of CaZrO_3 has been considered to be 5.0–6.0 eV, which is not experimentally proved at now. If the band structure obeys the rigid-band model exactly, E_F of CZ-Dry would be located at the valence band side since CZ-Dry is a p-type conductor. However, E_F is located at intermediate in the band gap. Thus, the observed energy shift seems to be small. This fact may reflect the band bending effect at the surface.^{9–11} It is known that the band at the surface of ordinary semiconductors bends downward in p-type semiconductor. This effect may depend on the space charge trapped by the surface state. Since CZ-Dry has a lot of oxygen defects, it is supported that the extra charge is trapped by defects at the surface. On the other hand, E_F of CZ-Wet is located at the conduction band side. This is consistent with the decrease in hole concentration by the exchange reaction between holes and hydrogen, $1/2 \text{H}_2 + h' = \text{H}$ (h' : hole and H: proton), proposed for the defect equilibrium in CaZrO_3 .

Figure 2 shows the PES spectra in the valence band energy region measured at $h\nu = 50$ and 90 eV. The top of the valence band of CZ-Wet is shifted by 1.0 eV to higher binding energy in order to compare the lineshape with that of CZ-Dry. The valence band spectra at $h\nu = 90$ eV show the density of state

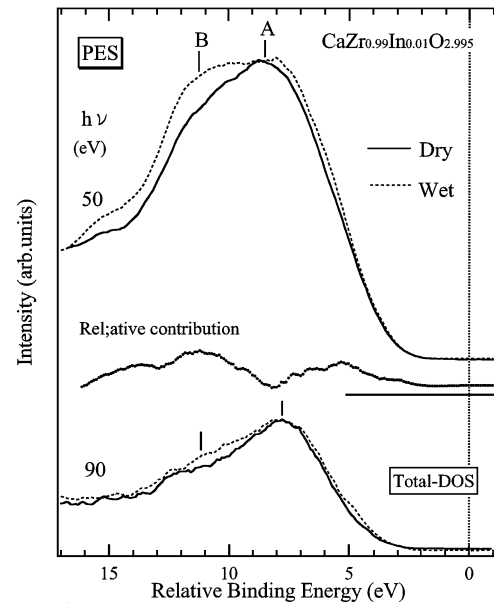
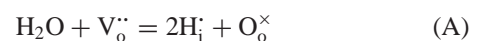


Fig. 2. Comparison of the photoemission spectra between CZ-Dry and CZ-Wet measured at $h\nu = 90$ and 50 eV. $h\nu = 90$ eV is cooper-minimum of Zr 4d cross section. The relative contribution is subtracted from CZ-Wet to CZ-Dry for $h\nu = 50$ eV.

(DOS), for almost O 2p, since for which there is a Cooper-minimum in the ionization cross-section of Zr 4d at this photon energy.¹³ The intensity of the bonding state at ~ 11 eV becomes strong because the ionization cross-section of Zr 4d increases with decreasing of photon energy, though that of O 2p also increases. Comparing the spectrum at $h\nu = 50$ eV, the intensity of the bonding state is stronger in CZ-Wet. The relative contribution, which is subtracted from CZ-Wet to CZ-Dry for $h\nu = 50$ eV, is also shown in Fig. 2. The contribution for CZ-Wet suggests that the hybridization effect between Zr 4d and O 2p states becomes stronger in CZ-Wet. Such the hybridization effect has been proved experimentally in SrTiO_3 and SrCeO_3 .^{9–11} In Sc-doped SrTiO_3 , it is indicated that the hybridization effect is closely related with the proton dissolution and resultant proton conductivity.¹¹ In all the perovskite proton conductors, the extent of the hybridization observed by PES spectra increased by the incorporation of protons. The proton conductivity of SrTiO_3 depends on Sc dopant concentration.¹⁴ Furthermore, the magnitude of the hybridization effect also changes with Sc doping.^{9,10} It is considered that the hybridization effect is closely related to the proton solubility and resultant emergence of proton conductivity in CaZrO_3 as well as SrTiO_3 , and SrCeO_3 .

The concentration of charge carriers can be estimated by the following defect chemical calculations. Since the predominant carrier changes among oxygen vacancy (oxide ion via vacancy mechanism), protons, and holes, depending on the atmosphere, the defect-chemical reactions for the formations of these predominant carriers for the CaZrO_3 system can be described, by employing Kröger-Vink notation,^{15,16} as follows.



The quasi-chemical equations are written using the equi-

librium constants for the reactions (A) and (B), $K_{(A)}$ and $K_{(B)}$ as,

$$K_{(A)} = [H_i]_i^2 [V_o^{..}] \cdot P_{H_2O}, \text{ and} \quad (1)$$

$$K_{(B)} = [H_i]_i^2 / C_p^2 \cdot P_{H_2}, \quad (2)$$

where square blankets with defect species denote the concentrations of hole and charged defects, which are expressed by the number of defects or holes per cm^{-3} . In addition, as the overall charge neutrality condition shown below (eq. (3)) holds, the concentration of ionic and electronic carriers can be estimated if the equilibrium constants are known.

$$2[V_o^{..}] + C_p + [H_i] = [In'_{Zr}] \quad (3)$$

The values of K_{OX} and K_H have been evaluated from the simultaneous measurements of total conductivity and Seebeck coefficient by employing a simple hopping conduction model for holes with the assumption that the density of state for the valence band is equal to that of oxide ions, and are expressed by the following equations,¹⁷⁾

$$K_{(A)} = 1.447 \times 10^{16} \exp(157, 631[J]/RT) \quad (4)$$

$$K_{(B)} = 3.043 \times 10^{-7} \exp(472, 140[J]/RT) \quad (5)$$

By solving eq. (1) through eq. (5), one can estimate the carrier concentrations of any species under a given set of temperature and partial pressures of H_2O and O_2 gas. The estimated values for CZ-Dry and CZ-Wet are tabulated in Table I.

In dry atmospheres, majority of the charge compensation is made by the formation of oxygen vacancy, and small deficiency in oxygen vacancy produces holes. Under wet atmospheres, the direct exchange reaction between H_2 and protons (reaction (B)) takes place in addition to the simple dissolution reaction of H_2O (reaction (A)), which results in the decrease of the C_p value by more than one order of magnitude.

From the above results, proton absorption mechanism might be described the schematic diagram as shown in Fig. 3. By In^{3+} doping, holes and oxygen vacancies exist in the crystal. When H_2O is absorbed at the surface, they exchange with proton and oxygen ion, indicating from Table I. These facts are indirectly supported from the shift of E_F , as is shown

Table I. Heat treatment conditions of two kinds (CZ-Dry and CZ-Wet) and the concentrations of protons, holes, and oxide ion vacancies estimated from the defect chemical calculation.⁹⁻¹¹⁾

| Sample Name | CZ-Dry | CZ-Wet | |
|------------------------------------|---------------------------------|--|-----------------------|
| Composition | $CaZr_{0.99}In_{0.01}O_{2.995}$ | $CaZr_{0.99}In_{0.01}O_{2.995}$ | |
| Anneal Gas | Dry O_2 | $O_2 + 0.03 \text{ vol\% } H_2O$ gas mixture | |
| Heat Treatment | 1523 K for 24 h | 1523 K for 24 h | |
| Concentration (cm^{-3}) | Proton $[H_i]$ | 0 | 1.53×10^{20} |
| | Hole C_p | 4.76×10^{18} | 1.70×10^{17} |
| | Oxygen | 7.52×10^{19} | 1.86×10^{18} |
| | Vacancy $[V_o^{..}]$ | | |

in Fig. 1. The binding energy of O 2p band, that is, increases by proton doping. On one hand, the process both [A] and [B] is important for the proton absorption mechanism. The bereaved problem is the hopping process (iii) between the oxygen-oxygen ions, which consist of an oxygen octahedron.⁶⁾ Although the process can not examine from this study, the hybridization effect between Zr 4d and O 2p states gives a large hint for the mechanism, as shown in Fig. 2. And, this effect may be a qualification to make proton stabilize in the crystal lattice.

In conclusion, we studied the relationship between the proton solubility and the electronic structure of protonic conductor $CaZrO_3$ using photoemission spectroscopy and defect chemical calculation. Comparing with the photoemission spectrum of CZ-Dry, E_F of CZ-Wet shifts to higher binding energy by about 1.0 eV, indicating the existence of proton that acts as positive charge. From the defect chemical calculation, it was clear that the hole and oxygen vacancy created by In^{3+} doping decreases by proton doping. These results prove that the doped-proton exchanges with hole and oxygen vacancy in the crystal lattice.

1) H. Iwahara, T. Esaka, H. Uchida and N. Maeda: Solid State Ionics 3-4 (1980) 359.

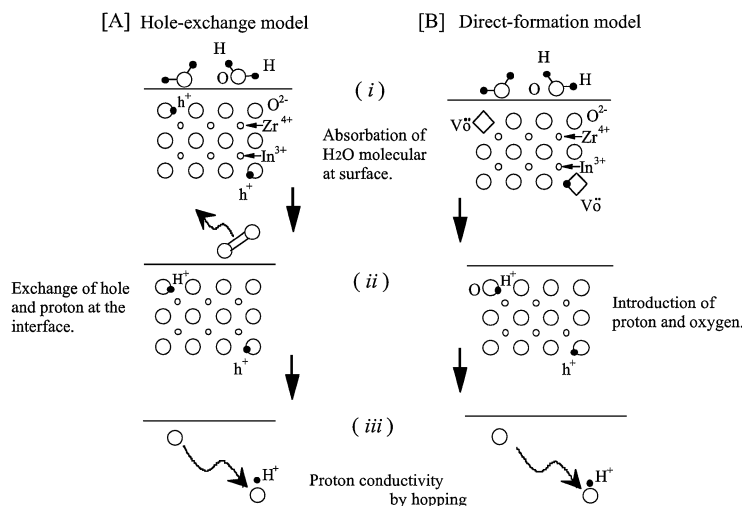


Fig. 3. Schematic diagrams for proton absorption mechanism. [A] Hole exchange (left): (i) H_2O is adsorbed on the surface. (ii) H_2O is resolved and proton is absorbed by exchange for hole. [B] Direct formation (right): (ii) proton and oxygen ion are introduced to the crystal. (iii) Proton migrates by hopping around oxygen ion.

- 2) S. Shin, H. H. Huang, M. Ishigame and H. Iwahara: *Solid State Ionics* **40/41** (1990) 910.
- 3) T. Yajima, H. Iwahara, N. Taketsu and K. Koide: *Kei-Kinzoku* **42** (1992) 263 [in Japanese].
- 4) N. Kurita, N. Fukatsu, K. Ito and T. Ohashi: *J. Electrochem. Soc.* **142** (1995) 1552.
- 5) K. Kobayashi: Dr. Thesis, Nagoya Institute of Technology, 1998.
- 6) N. Sata, K. Hiramoto, M. Ishigame, S. Hosoya, N. Niimura and S. Shin: *Phys. Rev. B* **54** (1996) 15795.
- 7) F. Shimojo, K. Hoshino and H. Okazaki: *J. Phys. Soc. Jpn.* **65** (1996) 1143.
- 8) N. Sata, M. Ishigame and S. Shin: *Solid State Ionics* **86** (1996) 629.
- 9) T. Higuchi, T. Tsukamoto, N. Sata, M. Ishigame, Y. Tezuka and S. Shin: *Phys. Rev. B* **57** (1998) 6978.
- 10) T. Higuchi, T. Tsukamoto, N. Sata, M. Ishigame, Y. Tezuka and S. Shin: *Solid State Ionics* **108** (1998) 349.
- 11) M. Matsumoto, K. Soda, K. Ichikawa, Y. Taguchi, K. Jouda, M. Kageyama, S. Tanaka, N. Sata, Y. Tezuka, S. Shin, S. Kimura and O. Aida: *J. Electron Relat. Phenom.* **78** (1996) 179.
- 12) S. Shin, A. Agui, Y. Tezuka, T. Ishii, Y. Minagawa, Y. Suda, A. Ebina, O. Mishima and K. Era: *Phys. Rev. B* **52** (1995) 11853.
- 13) J. J. Yeh and I. Lindau: *Atomic Data & Nuclear Data Tables* **32** (1993) 1.
- 14) K. Hiramoto: unpublished.
- 15) S. Yamaguchi, K. Kobayashi and Y. Iguchi: to be published in *Solid State Ionics* (1999).
- 16) K. Kobayashi, S. Yamaguchi and Y. Iguchi: *Solid State Ionics* **108** (1998) 355.
- 17) A. Kröger and H. J. Vink: *Solid State Physics*, eds. F. Seitz and D. Turnbull (Academic Press, New York, 1956) Vol. 3, p. 307.