

## Electronic Structure in the Bulk State of Protonic Conductor $\text{CaZrO}_3$ by Resonant Soft-X-Ray Emission Spectroscopy

Tohru HIGUCHI, Shu YAMAGUCHI<sup>1</sup>, Kiyoshi KOBAYASHI<sup>2</sup>, Tomoyuki TAKEUCHI, Shik SHIN<sup>3,4</sup> and Takeyo TSUKAMOTO

*Department of Applied Physics, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan*

<sup>1</sup>*Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

<sup>2</sup>*National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaragi 305-8565, Japan*

<sup>3</sup>*RIKEN, 1-1-1 Kouto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan*

<sup>4</sup>*Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*

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The electronic structure in the bulk state of the protonic conductor  $\text{In}^{3+}$ -doped  $\text{CaZrO}_3$  (CZI) has been investigated by resonant soft-X-ray emission spectroscopy (SXES), which reflects the electronic structure in the bulk state. The resonant SXES spectrum of proton-doped CZI shows a proton-induced level at the top of the valence band, indicating proton exchanges with holes. This finding confirms that protons exist in the bulk state, even though a surface state may also exist. [DOI: 10.1143/JJAP.41.L938]

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Perovskite-type oxides of general formula  $\text{ABO}_3$  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.<sup>1)</sup> Most attention has been focused on cerates and zirconates because of their excellent proton conductivity and chemical stability.<sup>2–8)</sup> In particular,  $\text{In}^{3+}$ -doped  $\text{CaZrO}_3$  (CZI) is the most practical material since the proton conductivity stabilizes at a relatively high temperature. From the defect chemical analysis, it has been estimated that the oxygen vacancies formed by a charge compensation reaction due to the substitution of  $\text{Zr}^{4+}$  for an acceptor dopant that has a lower valency than  $\text{Zr}^{4+}$ , are occupied partly by extraneous oxide ions under dry and oxidizing atmospheres and, as a result, holes form in the overall charge neutrality condition.<sup>7,8)</sup> Protons are incorporated by the dissolution of  $\text{H}_2\text{O}$  through the reaction with an oxygen vacancy and an oxide ion from two O–H groups and the direct exchange reaction between hole and proton. Furthermore, many theoretical and experimental investigations into the mechanism of proton migration have also been reported for perovskite-type protonic conductors.<sup>9–17)</sup>

In recent years, the electronic structure of  $\text{CaZrO}_3$  has been studied using photoemission spectroscopy (PES) and O 1s X-ray absorption spectroscopy (XAS).<sup>7,8)</sup> The Fermi level ( $E_F$ ) is about 1.0 eV higher because of proton doping, indicating the existence of a proton that acts as a positive charge. Furthermore, the intensities of the hole states at the top of the valence band and the acceptor-induced level just above  $E_F$  decrease with proton doping. These facts indicate that the doped proton exchanges with a hole and an oxygen vacancy in the crystal lattice. However, the exchange mechanism reflects the surface state.

In this Letter, we present the resonant soft-X-ray emission spectroscopy (SXES) spectra of dried and proton-doped CZI. Although photoemission spectroscopy (PES) has been a powerful method for studying the electronic structure, PES is surface-sensitive, because the mean free path of an electron is very short compared with that of light.<sup>18)</sup> Therefore, it is difficult to study the electronic structure of a thin film by PES as it requires a clean surface under ultrahigh vacuum. On the other hand, the SXES technique can investigate the electronic

structure of the bulk state, because the mean free path of a soft-X-ray is very long compared with that of an electron. Furthermore, the SXES has a clear selection rule regarding the angular momentum due to a dipole transition, as it occurs mainly within the same atomic species. Thus, we believe that the contribution of proton in the bulk state can be observed by O 1s  $\rightarrow$  2p SXES spectra.

The sample was a sintered ceramic prepared by a conventional solid-state reaction method. The starting materials were  $\text{ZrO}_2$  of 98% with 1.0 mass%  $\text{HfO}_2$  (99 mass% for  $\text{ZrO}_2 + \text{HfO}_2$ ) supplied by High Purity Chemicals Inc. and  $\text{CaCO}_3$  of 99.995 mass% and  $\text{In}_2\text{O}_3$  of 99.999 mass% purity supplied by Rare Metallic Co. Ltd. (Tokyo, Japan). The sample rods, prepared by isostatic pressing of well-mixed powder of the nominal composition of  $\text{CaZr}_{0.99}\text{In}_{0.01}\text{O}_{2.995}$ , were calcined at 1673 K for 10 h in air. Then, the samples were crushed to powder and mechanically pressed into disks. Finally, the disks were sintered at 1873 K for 10 h in air. The density of the disks was higher than 98% of the theoretical one calculated from the lattice parameter. The samples were confirmed as being of a single phase with the perovskite structure by powder X-ray diffraction analysis.

SXES spectra were measured using a soft-X-ray spectrometer installed at the undulator beamline BL-2C (at the Photon Factory), of the High Energy Accelerator Organization. Synchrotron radiation was monochromatized using a varied-line spacing plain grating whose average groove density is 1000 lines/mm. The incidence angle of the soft-X-ray was selected to be about 75° in order to avoid the self-absorption effect. The energy resolution was smaller than 0.4 eV at  $h\nu = 450$  eV. The bottom axis was calibrated by measuring the 4f core level of Au.

Figure 1(a) shows the O 1s XAS spectra of dried CZI. From the dipole selection rule, it is understood that the O 1s XAS spectra of the 4d transition metal oxide correspond to the transitions from O 1s to O 2p character hybridized into the unoccupied metal d states.<sup>7,19)</sup> The broad band at around  $\sim 534$  eV is attributed to the Ca 3d band that is mixed with unoccupied O 2p character. The peak at around  $\sim 529.5$  eV is the  $t_{2g}$  subband of the Zr 4d states: the  $e_g$ -subband is considered to be obscured by the overlapping Ca 3d bands. The vertical bars,

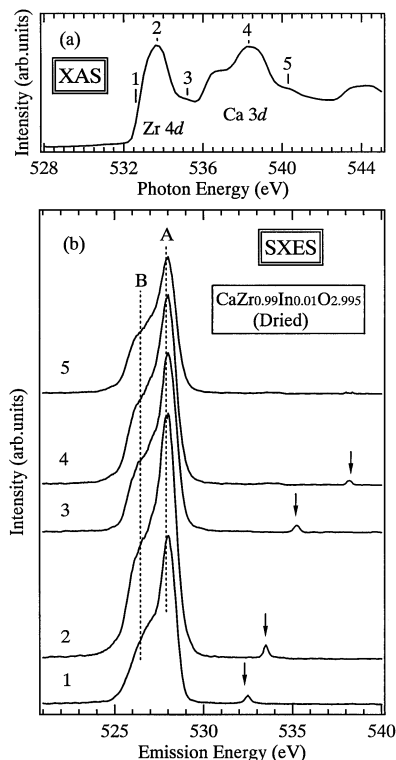


Fig. 1. (a) O 1s XAS spectrum of dried CZI. The numbers indicate the photon energies at which the resonant SXES spectra were measured. (b) O 1s SXES spectra of dried CZI excited at various photon energies indicated in Fig. 1(a). Arrows show the energy position of the excitation photon energy. A and B indicate the O 2p fluorescence components.

which are labeled from 1 to 5, indicate the selected photon energies from the resonant SXES measurements.

Figure 1(b) shows the O 1s resonant SXES spectra of dried CZI. The O 1s emission reflects the O 2p partial-density-of-state (PDOS) in the valence band region. An arrow shown in each spectrum indicates the excitation photon energy. The peak beneath the arrow is attributed to elastic scattering of the excitation photons. The elastic peak is enhanced at an excitation energy corresponding to the  $t_{2g}$  absorption peak and the intensity decreases with increasing photon excitation. A and B are observed at  $\sim 528.0$  eV and  $\sim 526.4$  eV, respectively. Although the intensity of the feature B does not depend on the photon excitation, that of the feature A is enhanced at the excitation energy corresponding to the  $t_{2g}$  absorption peak, indicating the O 1s  $\rightarrow$  2p resonance effect. However, the O 1s resonant SXES spectra are not found to exist by soft-X-ray Raman scattering, which is often useful observing in resonant SXES spectra excited at transition metal sites.<sup>18)</sup> Therefore, the O 1s resonant SXES spectra of CZI reflect the O 2p fluorescence component in the valence band region.

Figure 2(a) shows the comparison of the O 1s SXES spectra of dried and proton-doped CZI. The intensities of the SXES spectra are normalized by beam current and measurement time. By this normalization, the intensity of elastic scattering in dried CZI is in good agreement with that in proton-doped CZI. The line shape and bandwidth do not change in either spectra. The O 2p partial-DOS in the valence band mainly consists of two features, A and B. These energy positions accord with the PES spectra in the valence band of the same sample. Therefore, it is estimated that feature A corre-

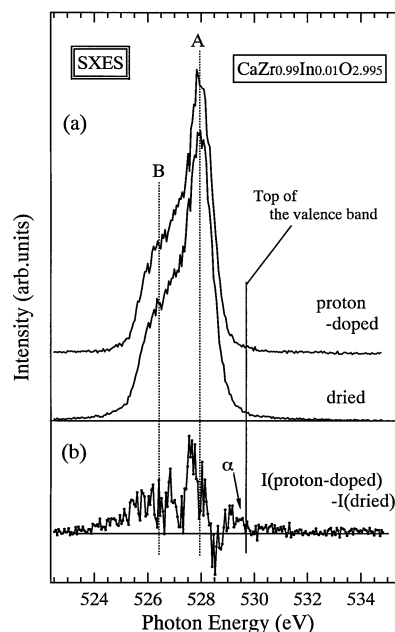


Fig. 2. (a) O 1s SXES spectra of dried and proton-doped CZI. This SXES spectrum of dried CZI is spectrum 2 in Fig. 1(b). (b) Difference SXES spectrum obtained by subtracting the O 1s SXES spectrum of dried CZI from that of proton-doped CZI. The vertical bar is the top of the valence band.

sponds to the nonbonding state and feature B corresponds to the bonding state that is well mixed with the Zr 4d states.

Figure 2(b) shows the difference spectrum by subtracting the O 1s SXES spectrum of dried CZI from that of proton-doped CZI. These features indicate the contribution of protons, which bond with oxygen ions (O-H bond). In the valence band region from 525 eV to 529 eV, the difference component in feature B (bonding state) is higher in proton-doped CZI. This result can be explained by the change of the hybridization effect between Zr 4d and O 2p states. From the resonant-PES (RPES) spectra at the Zr 4p  $\rightarrow$  4d absorption edge,<sup>8)</sup> it has been clarified that the Zr 4d partial-DOS of CZI in the valence band region increases with proton doping, indicating the increase of the hybridization effect. Thus, the O 2p partial-DOS observed from the SXES spectra in proton-doped CZI decreases, which is in contrast to the results of a resonant-photoemission study, since the total DOS in the valence band does not change in either spectra. On the other hand, the difference component in feature A indicates the existence of protons in the nonbonding state.

It is striking that an apparent feature corresponding to the  $\alpha$  peak is observed at the top of the valence band. A similar result has been observed in the O 1s X-ray absorption spectroscopy (XAS) spectra.<sup>7,20)</sup> In dried CZI, the XAS spectrum below the O 1s threshold shows two empty features whose energy positions match the hole state at the top of the valence band and the acceptor level above the Fermi level ( $E_F$ ). However, the intensities of 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 replace the holes and oxygen vacancies in the crystal lattice. On the other hand, a tiny feature is observed at about 0.7 eV above the top of the valence band, although the feature

is very weak in Fig. 2(b). If the existence of the feature is clarified by careful measurement using high-resolution and high-brightness SXES, the energy separation between the  $\alpha$  peak and the feature might be related to the activation energy for the migration of protons, which is estimated for the analysis of the ionic part of the Seebeck coefficient<sup>7)</sup> and the quantum mechanical molecular dynamics simulation based upon the density functional theory.<sup>9, 10)</sup> Thus, the above results indicate that protons act as positive charges in the bulk state.

In conclusion, we have studied the electronic structure in the bulk state of protonic conductor CZI using SXES. In proton-doped CZI, the existence of a proton-induced state was observed at the top of the valence band. This finding proves that the proton acts as a positive charge in the bulk state. These findings are direct evidence that protons exist in the bulk state, even though a surface state may also exist.

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- 1) H. Iwahara, T. Esaka, H. Uchida and N. Maeda: *Solid State Ionics* **3/4** (1980) 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.
- 4) N. Sata, K. Hiramoto, M. Ishigame, S. Hosoya, N. Niimura and S. Shin: *Phys. Rev. B* **54** (1996) 15795.
- 5) T. Higuchi, T. Tsukamoto, N. Sata, K. Hiramoto, M. Ishigame and S. Shin: *Jpn. J. Appl. Phys.* **40** (2001) 4162.
- 6) K. Kobayashi, S. Yamaguchi and Y. Iguchi: *Solid State Ionics* **108** (1998) 355.
- 7) S. Yamaguchi, K. Kobayashi, T. Higuchi, S. Shin and Y. Iguchi: *Solid State Ionics* **136/137** (2000) 305.
- 8) T. Higuchi, T. Tsukamoto, Y. Tezuka, K. Kobayashi, S. Yamaguchi and S. Shin: *Jpn. J. Appl. Phys.* **39** (2000) L 133.
- 9) M. S. Isram, R. A. Davies and J. D. Gale: *Chem. Mater.* **13** (2001) 2049.
- 10) M. S. Isram: *J. Mater. Chem.* **10** (2000) 1027.
- 11) F. Shimojo, K. Hoshino and H. Okazaki: *J. Phys. Soc. Jpn.* **66** (1997) 8.
- 12) F. Shimojo, K. Hoshino and H. Okazaki: *J. Phys. Soc. Jpn.* **67** (1998) 2008.
- 13) Z. Q. Li, J. L. Zhu, C. Q. Wu, Z. Tang and Y. Kawazoe: *Phys. Rev. B* **58** (1998) 8075.
- 14) S. Matsuo, H. Yugami and M. Ishigame: *Phys. Rev. B* **64** (2001) 24302.
- 15) N. Sata, S. Shin, K. Shibata and M. Ishigame: *J. Phys. Soc. Jpn.* **68** (1999) 3600.
- 16) O. Kamishima, K. Ohta, Y. Chiba and T. Hattori: *J. Phys. Condens. Matter* **11** (1999) 5355.
- 17) N. Sata, H. Sone, N. Kitamura, T. Hattori and M. Ishigame: *Solid State Ionics* **136/137** (2000) 197.
- 18) T. Higuchi, T. Tsukamoto, M. Watanabe, M. M. Grush, T. A. Callcott, R. C. Perera, D. L. Ederer, Y. Tokura, Y. Harada, Y. Tezuka and S. Shin: *Phys. Rev. B* **60** (1999) 7711.
- 19) T. Higuchi, T. Tsukamoto, K. Kobayashi, S. Yamaguchi, N. Sata, M. Ishigame, Y. Ishiwata and S. Shin: *Phys. Rev. B* **65** (2002) 33201.
- 20) T. Higuchi, T. Tsukamoto, K. Kobayashi, S. Yamaguchi, N. Sata, M. Ishigame, Y. Ishiwata and S. Shin: *Solid State Ionics* **136/137** (2000) 261.