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Short Note

Optical Absorption Spectra of Protonic Conductor $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$

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The fundamental absorption edge of protonic conductor Sc-doped $CaZrO_3$ ($CaZr_{0.95}Sc_{0.05}O_{3-\delta}$) was firstly measured by optical absorption spectroscopy in the vacuum ultraviolet region. In dry-annealed $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$, a large absorption structure was observed at ~0.7 eV from the top of the valence band of wet-annealed $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$. The intensity is lower in wet-annealed $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$. This finding indicates that the doped protons are exchanged with holes or oxygen vacancies, which are formed by Sc^{3+} doping. [DOI: 10.1143/JJAP.42.1331]

KEYWORDS: $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$, protonic conductor, optical absorption spectra, hole, oxygen vacancy

Some perovskite-type oxides, such as $SrZrO_3$, $CaZrO_3$ and $SrTiO_3$, exhibit remarkable protonic conductivity when they are doped with a few mol% of acceptor ions.[1–6] These protonic conductors are important materials for a wide variety of electrochemical applications such as fuel cells and hydrogen sensors in the renewable energy-source industry. Since proton-conducting perovskite oxides were discovered by Iwahara *et al.*,[1] various investigations have been made to clarify their origin and nature.[7–17] In particular, acceptor-doped $CaZrO_3$ is the most practical protonic conductor because of its excellent protonic conductivity and chemical stability at relatively high temperature. The transport properties have been extensively studied by Kobayashi *et al.*,[8] Yamaguchi and co-workers,[9–11] and Higuchi and co-workers.[12,13] They reported that the predominant charge carrier can be varied among protons, and oxide ions and holes by temperature, oxygen and hydrogen pressures in the atmosphere. Protons are incorporated by the dissolution of H_2O by the reaction with an oxygen vacancy and an oxide ion to form two O–H groups and the direct exchange reaction between hole and hydrogen.

In recent years, the electronic structure of protonic conductor In^{3+}-doped $CaZrO_3$ (CZI) has been investigated by soft-X-ray emission spectroscopy (SXES).[13] The SXES spectrum shows a proton-induced level at the top of the valence band, indicating that protons exchange with holes or oxygen vacancies. Furthermore, a very small feature is also observed near 0.7 eV from the top of the valence band. The energy separation between the top of the valence band and the very small 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.[10]

To further investigate the mechanism of protonic conduction, the electronic structure near the fundamental absorption edge of $CaZrO_3$ should be clarified. However, this structure has not been reported thus far. Here, the authors report the optical absorption spectra in the vacuum ultraviolet region of protonic conductor Sc^{3+}-doped $CaZrO_3$ ($CaZr_{0.95}Sc_{0.05}O_{3-\delta}$).

The sample was a single crystal of $CaZrO_3$ doped with 5 mol% Sc^{3+} on the Zr^{4+} site, which was grown by the floating-zone method using a Xe-arc imaging furnace using the powdery material prepared by a solid-state reaction of $CaCO_3$, ZrO_2, and Sc_2O_3 calcined at 1200°C for approximately 12 h. The single crystal was grown in pure oxygen atmosphere to prevent water pick-up. The prepared crystal was transparent and the dimensions of the rod were approximately 2–3 mm diameter and ~20 mm length. The crystal was examined using X-ray diffraction and the Laue method. The dopant concentration was 5 mol%. The crystal was annealed in an atmosphere of saturated H_2O vapor pressure at 20°C for 3 h in order to introduce protons into the crystal. In the case of dry-annealed, the crystal was annealed in an atmosphere of N_2 vapor pressure at 800°C for 3 h in order to prevent the protons from entering the crystal.

Optical absorption measurement in the vacuum ultraviolet region has been carried out at the BL-1 installed at the Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo. The absorption spectra were measured in the energy region from 2 to 7 eV. The beam size was approximately 1 × 2 mm. The single crystal samples were polished into a thin plate with a thickness of 69 μm and fixed on a sample holder with silver paste. The measurement temperature was about 90 K.

Figure 1 shows the comparison of the optical absorption spectra at the fundamental absorption edge of dry-annealed and wet-annealed $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$ samples. The funda-

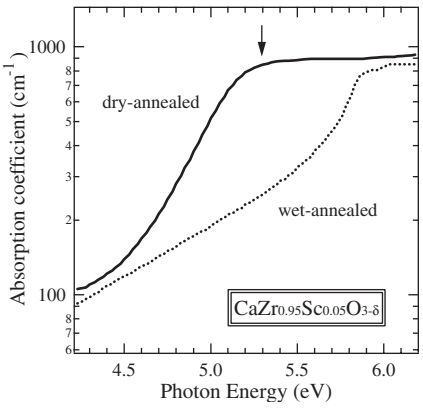

Fig. 1. Absorption spectra of dry-annealed (solid line) and wet-annealed (dashed line) $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$ around the fundamental absorption edge at low temperature.

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mental absorption edge corresponds to the transition from the O $2p$ valence band to the Zr $4d$ conduction band. The absorption coefficients of dry-annealed and wet-annealed $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$ samples are the highest at ~5.3 eV and ~6.0 eV, respectively, in this energy region. The top of the valence band is considered to be located at ~6.0 eV. This finding indicates that dry-annealed $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$ has a large absorption structure at ~5.3 eV, as shown by the arrow. Therefore, the value of the absorption edge cannot be determined from the Urbach tail. The existence has also been observed in the optical absorption spectra of Y^{3+}-doped $SrZrO_3$.[7] However, the absorption structure is not found in Sc^{3+}-doped $SrTiO_3$ or in undoped $SrZrO_3$. Therefore, the existence of the absorption band might be a unique structure for acceptor-doped zirconate. In the absorption spectra of Y^{3+}-doped $SrZrO_3$, the energy shift of the absorption edge due to Y^{3+} doping was observed and the band gap was found to increase with increasing Y^{3+} dopant concentration. Therefore, it is suggested that holes are formed at the top of the valence band due to Y^{3+} doping.[7]

In recent years, the electronic structure of CZI has been investigated by O $1s$ X-ray absorption spectroscopy (XAS).[10,11] On the basis of the dipole selection rule, it has been understood that the O $1s$ XAS spectrum corresponds to a transition from O $1s$ to the unoccupied O $2p$ character. Below the O $1s$ threshold, the XAS spectra of dry-annealed CZI show an empty state whose energy position matches with the top of the valence band. The empty state indicates the existence of a hole that is formed at the top of the O $2p$ valence band due to In^{3+} doping. The intensity of the hole decreases with proton doping, indicating that doped protons are exchanged with holes or oxygen vacancies at the top of the valence band formed by In^{3+} doping. This behavior accords with the results of Fig. 1 and the photoemission study,[12] though the dopant ion is different from the sample used in this study. The origin of the 5.3 eV absorption structure in Fig. 1 has not been clarified thus far. However, the absorption band at ~5.3 eV is thought to be a hole or acceptor-induced level that contributes to the oxygen components. On the other hand, the increase of the absorption coefficient in dry-annealed $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$ above ~4.6 eV might indicate the existence of an other absorption structure such as a O $2p$ defect-induced level. The existences of hole, acceptor- and defect-induced levels are in good accordance with the results of the SXES study[13] and the calculation based upon both interatomic potential and quantum mechanical methods by Islam *et al.*[17]

In conclusion, we studied the electronic structure near the fundamental absorption edge of protonic conductor $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$ using optical absorption spectroscopy in the vacuum ultraviolet region. The optical absorption spectrum of dry-annealed $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$ exhibits a large absorption structure at ~0.7 eV from the top of the valence band in wet-annealed $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$. The intensity of the absorption structure is lower in wet-annealed $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$. This fact indicates that the doped proton exchanges with a hole or oxygen vacancy in $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$.

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