

A Study on the Electronic Structure of Proton Conducting $A^{III}B^{III}O_3$ Single Crystal

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Introduction

Since it was reported in the early 1980s that some acceptor-doped ABO_3 perovskite-type oxides such as $A^{II}B^{IV}O_3$ ($SrCeO_3$, $BaCeO_3$ and others) show high proton conductivity in a humid atmosphere at high temperatures, studies of high-temperature proton conductors have become more intensive because of their potential applications in fuel cells or hydrogen sensors. Recently some acceptor-doped $A^{III}B^{III}O_3$ perovskite-type oxides such as $LaSc_{0.8}Mg_{0.2}O_3$, $La_{0.9}Sr_{0.1}LuO_3$, $La_{0.9}Sr_{0.1}YO_3$ and others have also been reported to show high proton conductivity in the presence of H_2O vapor or hydrogen at high temperatures. Among them, the $La_{0.8}Sr_{0.2}ScO_3$ ceramic shows the highest proton conductivity, comparable to that of $BaCe_{0.95}Y_{0.05}O_3$. These results suggest that Sr-doped $LaScO_3$ oxides are promising proton conductors. However, their proton conducting mechanism has not yet been fully studied and their fundamental physical and chemical properties need clarification.

In this study, the electronic structure near the bottom of the conduction band and the top of the valence band for $La_{1-x}Sr_xScO_3$ single crystal ($x = 0.03$; denoted by LSS3) annealed under wet atmosphere at $800^\circ C$ has been investigated by X-ray absorption spectroscopy (XAS).

Experimental

A transparent LSS3 crystal was grown by the floating zone method in a Xe arc imaging furnace. XAS spectrum was measured using a soft-X-ray spectrometer installed at the undulator beamline BL-19B of the Photon Factory at the High Energy Accelerator Organization. The photon energy was calibrated by measuring the photoemission spectrum of the $4f$ core level of an Au film. The single crystal was cut into a plate shape with a thickness of about 0.5 mm, and the surface was optically polished. Before measurement, the sample was annealed at $800^\circ C$ for 10 h in wet air ($Ar:O_2 = 4:1$, $P_{H_2O} = 3$ kPa).

Results and discussion

Fig. 1 shows the O $1s$ XAS spectrum of the LSS3 single crystal annealed at $800^\circ C$ in the wet atmosphere. Based on the dipole selection rule, it can be understood that the O $1s$ XAS spectrum for ScO_6 -octahedral structures corresponds to transitions from the O $1s$ to the O $2p$ state hybridized with the unoccupied Sc $3d$ states. The absorption edge around 532 eV is mainly composed

of the t_{2g} -subband of the unoccupied Sc $3d$ state hybridized with the O $2p$ state. The absorption at ~ 536 eV is considered to correspond to the Sc $3d$ and La $5d$ states. An obvious absorption feature appears at ~ 531 eV for LSS3 below the Sc $3d$ absorption edge, which is not observed for an undoped $LaScO_3$ single crystal. The feature is considered to be due to oxygen vacancies induced by Sr doping.

The XAS spectrum of wet-annealed LSS3 shows broad absorption around the top of the valence band. Many studies on the electronic structure near the band gap region in perovskite-type oxide based proton conductors have been done. Sata *et al.* investigated the electronic structure of p-type $SrTiO_3$ and Y-doped $SrZrO_3$ in the UV/Vis region using optical absorption spectroscopy. It has been suggested that holes are formed at the top of the valence band due to acceptor doping, and that the holes or oxygen vacancies can be replaced by protons or hydroxide ions, respectively. These absorptions derived from holes in O $1s$ XAS spectrum were also observed in other acceptor-doped $A^{II}B^{IV}O_3$ perovskite-type oxides; however, absorption due to holes in the valence band has not been observed in acceptor-doped $A^{III}B^{III}O_3$ perovskite-type oxides. In the O $1s$ XAS spectrum of LSS3, the absorption related to the holes is observed not in dry-annealed sample but in wet-air-annealed one. The difference in hole creation may be due to the differences in electronic structure between $A^{II}B^{IV}O_3$ and $A^{III}B^{III}O_3$.

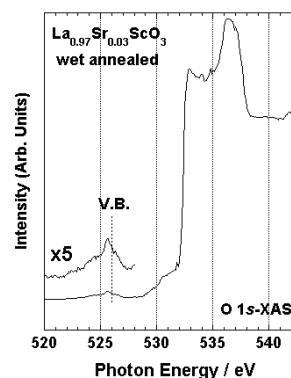


Fig. 1. O $1s$ XAS spectrum of LSS3 single crystal measured at room temperature after annealing at $800^\circ C$ in wet atmosphere. Vertical dashed line indicates the top of the valence band (V.B.).

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