

Electronic structure of BaPrO₃-based oxides studied with soft X-ray absorption and emission spectroscopy

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Introduction

Solid Oxide Fuel Cells (SOFCs) employing proton-conducting oxides as electrolyte is expected as a way to realize low-temperature operation. Compared with numerous studies on proton-conducting oxides as the electrolytes, one may find less investigations on the cathode materials for proton-conducting SOFC (PC-SOFC). It is considered that proton-hole (or electron) mixed conductivity is an important property for high cathode performance.

In the precedent studies, we evaluated the electrochemical properties of BaPr_{1-x}Yb_xO₃ in expectation of proton-hole mixed conduction [1]. Against the expectation, its proton solubility was found to be quite small. On the other hand, the oxide shows predominant hole conductivity, which increases almost linearly with the dopant concentration, but the conductivity itself is very low. While the observed conduction behavior appears to follow a classic defect-chemical scheme and rigid-band model, we have recently found anomalous electronic structures via X-ray spectroscopies. In this paper, we report the results of X-ray spectroscopies, emphasizing a strong correlation between trivalent Pr and hole/proton.

Results and discussion

Figure 1 shows the O1s-2p and Pr3d-4f X-ray Absorption (XAS) spectra, which reflect respective partial unoccupied density of state. While only an unoccupied state corresponding to the conduction band (A) is observed in the Pr3d-4f XAS (Fig. 1(ii)), another peak below the conduction band (B) is prominent in the O1s-2p XAS (Fig. 1(i)). Therefore, the additional peak (B) corresponds to a non-bonding O2p level doped with hole, which is generated together with trivalent Pr³⁺ via an auto-ionization reaction. The latter is confirmed by the presence of an occupied state pairing with feature (B) observed with RIXS using O2p resonance.

It should be noted that the additional level (B) corresponding to the hole exists even in undoped BaPrO₃, which shows poor electric conductivity as reported in the previous study [1]. Furthermore, DOS of the additional level (B) tends to decrease upon Yb-doping, while the hole conductivity increases at the same time [1]. These results may suggest that, although appreciable concentrations of electron holes exist in lightly- or undoped BaPrO₃, they are strongly attracted to trivalent Pr

via electrostatic force. Therefore, such holes can not contribute to electronic conductivity. The positive dependence of total conductivity upon Yb-concentration can be attributed to the formation of another hole state (C), probably formed by the dopant, which is observed in the O1s-2p XAS (Fig. 1(i)) of heavily doped samples.

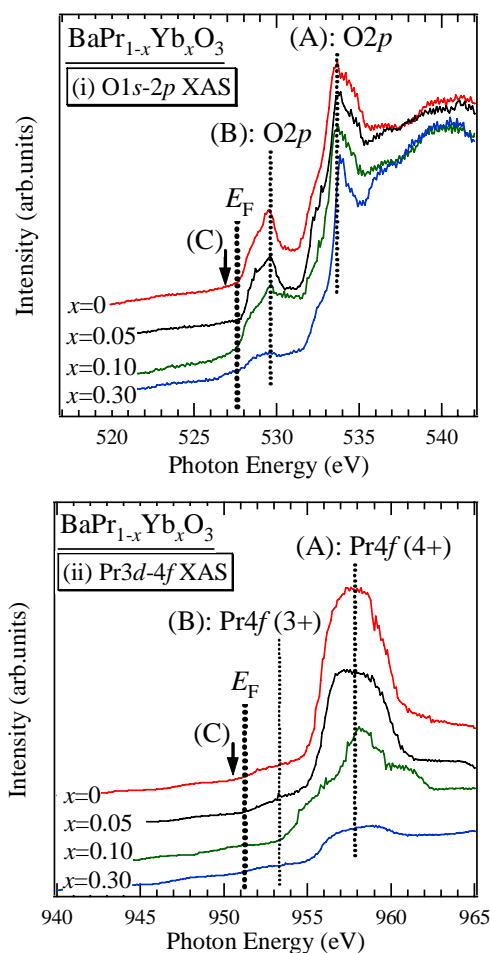


Fig. 1. O1s-2p (i) and Pr3d-4f (ii) XAS spectra of BaPr_{1-x}Yb_xO₃.

References

- [1] S. Mimuro et al., Solid State Ionics 178, 641 (2007).

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