

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 are expected as new energy conversion device with high efficiency. While numerous studies have been devoted to proton-conducting oxides as the electrolytes, there have been fewer reports on the proton-electronic mixed-conducting materials for cathodes of proton-conducting SOFCs.

In our previous studies, the electrochemical properties of BaPr_{1-x}Yb_xO₃ have been investigated in expectation of proton-hole mixed conductivity [1]. Actually, the oxide shows predominant hole conductivity rather than protonic one. While the observed conduction behaviour appears to follow a classic defect-chemistry, we have recently found anomalous electronic structures via X-ray spectroscopy [2]. It has been inferred that both of the unoccupied state which corresponds to a non-bonding O2p level doped with hole (O[•]) and the occupied state which corresponds to Pr³⁺ simultaneously decreases in intensity upon doping with Yb. Therefore, it is considered that the two defect species O[•] and Pr³⁺ generate together via an auto-ionization reaction: Pr⁴⁺ + O²⁻ → Pr³⁺ + O[•].

In this report, we present the results of soft X-ray spectroscopy on Ba_{0.95}La_{0.05}PrO₃, in which La³⁺ should act as a donor, in order to further understand the overall picture of the electric transport property as well as electronic structure in the BaPrO₃-based system.

Manuscript preparation

Figure 1 shows the O1s-2p and Pr3d-4f X-ray Absorption (XAS) spectra of BaPrO₃ (BP), Ba_{0.95}La_{0.05}PrO₃ (BLP5), and BaPr_{0.7}Yb_{0.3}O₃ (BPY30), which reflect respective partial unoccupied density of state. In the O1s-2p XAS (Fig. 1 (a)), as has been observed for BaPr_{1-x}Yb_xO₃, a pre-edge peak (A) has been observed at 534 eV, which is attributed to an unoccupied non-bonding O2p level, O[•]. The peak (A) of BPY is smaller in intensity than that of BP, which corresponds to the decrease in the hole concentration by the auto-ionization. Another important observation is that in the spectrum of BPY30, a shoulder (B) is observed at the low energy side of the peak (A). Since the hole conductivity of BaPr_{1-x}Yb_xO₃ increases with x [1], it is deduced that the unoccupied state (B) corresponds to the electron holes introduced by Yb³⁺-doping. Thus the two hole states originating from auto-ionization and chemical doping of Yb have been distinguished. On the other hand, no

significant difference can be found between the O1s-2p XAS spectra of BP and BLP5, indicating that the carriers introduced by La-doping are electrons. The Pr3d-4f XAS spectra (Fig. 1(b)) shows almost no difference between the compositions, indicating that the charge compensation for acceptor(Yb)-doping is mostly taken by contributed to by oxygen rather than praseodymium.

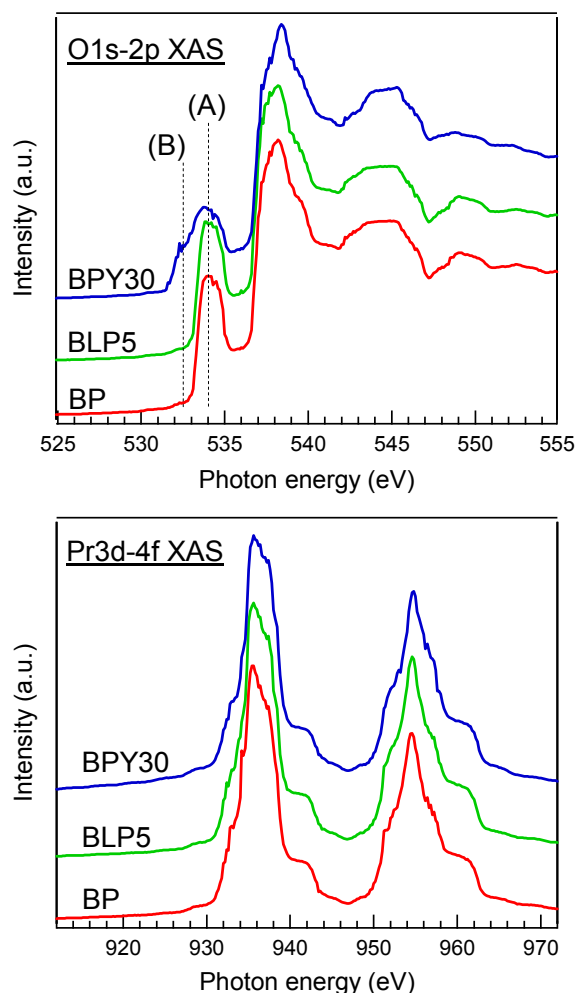


Fig. 1: O1s-2p (a) and Pr3d-4f (b) XAS spectra of BP, BPY30 and BLP5.

References

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